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Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options. Volume XX: Toxics/Organics

Arthur D. Little, Inc., Cambridge, MA

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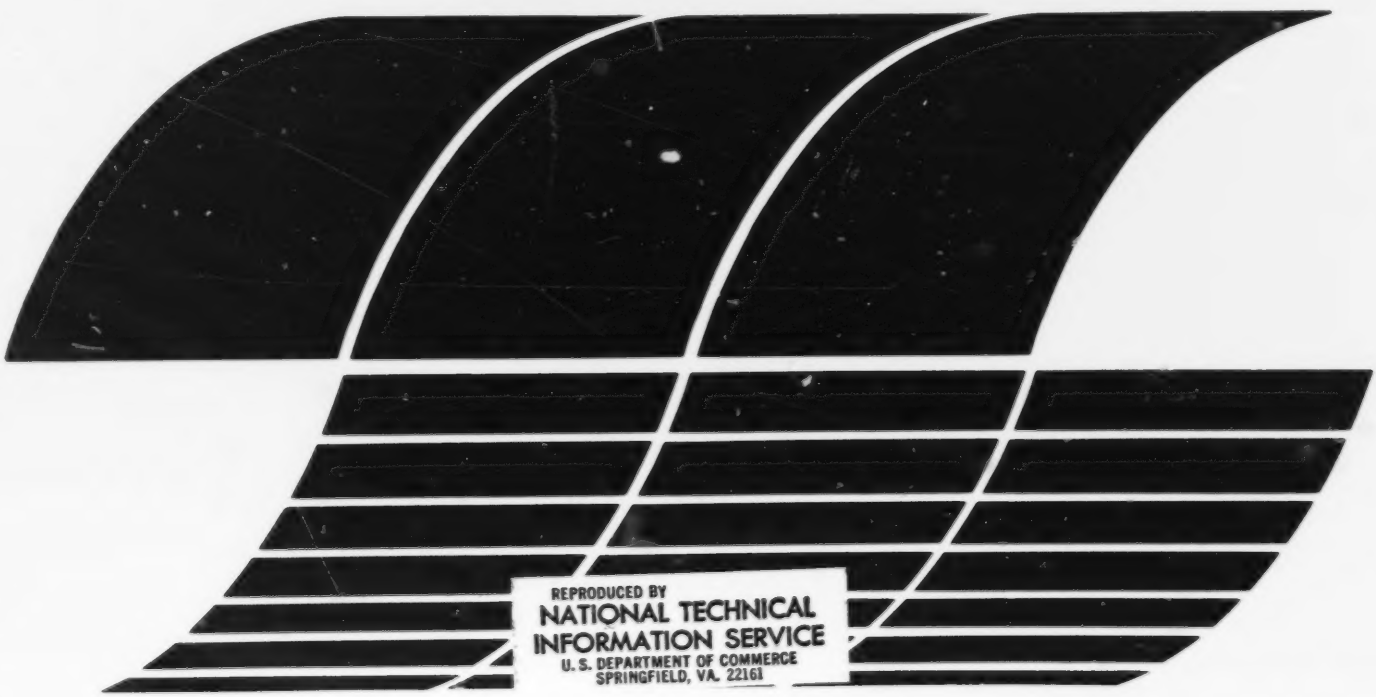
Volume XX
Toxics/Organics

Interagency Energy/Environment R&D Program Report



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This present report summarizes the information regarding toxic/organic pollutants in the 13 industry reports. Four parallel reports treat sulfur oxides, nitrogen oxides, particulates, and solid residues. All of these pollutant oriented reports are intended to be closely used with the original 15 reports.

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ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY-CONSERVING MANUFACTURING PROCESS OPTIONS

Volume XX. Toxics/Organics

by

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Contract No. 68-03-2198

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment, and even on our health, often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report summarizes information on toxics/organics from a study of 13 energy-intensive industries. If implemented over the coming 10 to 15 years, these processes and practices could result in more effective utilization of energy resources. The study was carried out to assess the potential environmental/energy impacts of such changes and the adequacy of existing control technology in order to identify potential conflicts with environmental regulations and to alert the Agency to areas where its activities and policies could influence the future choice of alternatives.

The results will be used by the EPA's Office of Research and Development to define those areas where existing pollution control technology suffices, where current and anticipated programs adequately address the areas identified by the contractor, and where selected program reorientation seems necessary.

Specific data will also be of considerable value to individual researchers as industry background and in decision-making concerning project selection and direction.

The Power Technology and Conservation Branch of the Energy Systems-Environmental Control Division should be contacted for additional information on the program.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Under EPA Contract No. 68-03-2198, Arthur D. Little, Inc. undertook a study of the "Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options." Some 80 industrial process options were examined in 13 industrial sectors. Results were published in 15 volumes, including a summary, industry prioritization report, and 13 industry oriented reports (EPA-600/7-76-034 a through o).

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ENGLISH-METRIC (SI) CONVERSION FACTORS

To Convert From	To	Multiply By
Acre	$Metre^2$	4,046
Atmosphere (normal)	Pascal	101,325
Barrel (42 gal)	$Metre^3$	0.1589
British Thermal Unit	Joule	1,055
Centipoise	Pascal-second	0.001
Degree Fahrenheit	Degree Celsius	$t_C^o = (t_F^o - 32)/1.8$
Degree Rankine	Degree Kelvin	$t_K^o = t_R^o/1.8$
Foot	Metre	0.3048
$Foot^3$/minute	$Metre^3$/sec	0.0004719
$Foot^3$	$Metre^3$	0.02831
$Foot^2$	$Metre^2$	0.09290
Foot/sec	Metre/sec	0.3048
$Foot^2$/hr	$Metre^2$/sec	0.00002580
Gallon (U.S. liquid)	$Metre^3$	0.003785
Horsepower (550 ft-lbf/sec)	Watt	745.7
Horsepower (electric)	Watt	746.0
Horsepower (metric)	Watt	735.5
Inch	Metre	0.02540
Kilowatt-hour	Joule	3.60×10^6
Litre	$Metre^3$	1.000×10^{-3}
Micron	Metre	1.000×10^{-6}
Mil	Metre	0.00002540
Mile (U.S. statute)	Metre	1,609
Poise	Pascal-second	0.1000
Pound force (avdp)	Newton	4.448
Pound mass (avdp)	Kilogram	0.4536
Ton (Assay)	Kilogram	0.02916
Ton (long)	Kilogram	1,016
Ton (metric)	Kilogram	1,000
Ton (short)	Kilogram	907.1
Tonne	Kilogram	1,000

Source: American National Standards Institute, "Standard Metric Practice Guide," March 15, 1973. (ANS72101-1973) (ASTM Designation E380-72)

SECTION 1

INTRODUCTION

BACKGROUND AND PURPOSE

During 1975 and the first half of 1976, under EPA Contract No. 68-03-2198, Arthur D. Little, Inc., undertook a study of the "Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options" in 13 energy-intensive industry sectors for the U.S. Environmental Protection Agency (EPA). The results of these studies were published in the following reports:

- Volume I -- Industry Summary Report (EPA-600/7-76-034a)
- Volume II -- Industry Priority Report (EPA-600/7-76-034b)
- Volume III -- Iron and Steel Industry (EPA-600/7-76-034c)
- Volume IV -- Petroleum Refining Industry (EPA-600/7-76-034d)
- Volume V -- Pulp and Paper Industry (EPA-600/7-76-034e)
- Volume VI -- Olefins Industry (EPA-600/7-76-034f)
- Volume VII -- Ammonia Industry (EPA-600/7-76-034g)
- Volume VIII -- Alumina/Aluminum Industry (EPA-600/7-76- 034h)
- Volume IX -- Textiles Industry (EPA-600/7-76-034i)
- Volume X -- Cement Industry (EPA-600/7-76-034j)
- Volume XI -- Glass Industry (EPA-600/7-76-034k)
- Volume XII -- Chlor-Alkali Industry (EPA-600/7-76-034l)
- Volume XIII -- Phosphorus/Phosphoric Acid Industry (EPA-600/7-76-034m)
- Volume XIV -- Copper Industry (EPA-600/7-76-034n)
- Volume XV -- Fertilizer Industry (EPA-600/7-76-034o)

In the course of this study some 80 industrial process options were examined, focusing on:

- Identification of any major sources and amounts of pollutants (air, water, and solid) expected from the processes;
- Development of estimated capital and operating costs for both production and pollution control aspects of the processes;
- Estimation of the types and amounts of energy used in both production and pollution control for the processes;
- Assessment of the economic viability and likelihood of implementation of those alternative process options being studied;
- Identification of areas where EPA's activities and policies could influence the future choice of alternatives; and
- Identification of research and development areas in both process and pollution control technology.

Because of the industry orientation of the study, encompassing fifteen volumes and some 1,700 pages, it was felt that pollutant-specific information across all the 13 sectors studied should be summarized so that environmental, energy and economic impacts can be considered from this viewpoint. Five such pollutant types were identified as being of particular interest:

- Nitrogen oxide (NO_x) emissions,
- Sulfur oxide (SO_x) emissions,
- Fine particulate emissions,
- Solid residues, and
- Organic and/or toxic pollutants.

A summary pollutant report in each of these areas has been prepared. Although we did attempt some estimates and extrapolations on pollutants where the information was readily available, in general, we did not attempt to go beyond the contents of the 15 original reports.

APPROACH

These summary pollutant reports are intended to be used closely with the original 15 reports. Generally, information such as detailed descriptions of the processes has not been duplicated in these pollutant reports. Sections of the previous 15 reports where this information can be found have been extensively referenced by volume number and page number (e.g., Volume VII, page 20, refers to page 20 of the Ammonia Industry report).

In Section 2 of this report (Findings and R&D Overview), summary information on generic, cross-industry problems that emerged and suggestions for research and development work in the areas of both pollution control technology and process technology are presented. In Section 3 of this report, the subject of "toxic/organic pollutants" is reviewed in relation to the industries and processes analyzed in the original study. All emissions are estimated unless specifically referenced, since we believe that actual data do not exist for many of the processes described, which are frequently still under development. The significance of pollution in terms of specific organics and toxic constituents is a relatively new concept and historical data simply have not been collected in most industries.

To give the reader a sense of the size of the industries for which the pollution problems covered in these summary pollutant reports are considered, Table 1 lists these industries, their total production in 1974 (the base case year for the study), and their projected incremental production in 1989, 15 years hence. Other than the estimates given in this report, reliable pollutant loads, in terms of organics and/or toxics, have yet to be developed on a parallel basis.

TABLE 1. PROJECTED U.S. PRODUCTION IN INDUSTRIES STUDIED

Commodity	Total U.S. production in 1974 (10^6 tons*)	Projected rate of growth (%/yr)	Total projected production in 1989 (10^6 tons)	Increase in annual production in 1989 over that of 1974 (10^6 tons)
Alumina	7.7	6.0	18.5	10.75
Aluminum	5.0	6.0	12.0	7.0
Ammonia	9.2	6.0	22.0	12.8
Cement	79.0	2.0	106.3	27.3
Chlorine	11.0	5.0	22.9	11.9
Coke	62.0	2.5	89.8	27.8
Copper	1.6	3.5	2.7	1.1
Fertilizers (HNO_3)	8.2	4.0	14.8	6.6
Glass (flat)	29.0	2.5	42.0	13.0
Iron	100.0	2.5	144.8	44.8
Olefins (ethylene)	13.0	8.0	41.2	28.2
Petroleum	740.0**	1.5	925.0***	185.0****
Pulp (kraft)	16.0	5.0	33.3	17.3
Pulp (newsprint)	3.9	2.5	5.6	1.7
Phosphoric Acid (detergent grade)	1.4	2.5	2.03	0.63
Phosphoric Acid (wet acid grade)	9.0	2.5	13.0	4.0
Steel	133.0	2.5	193.0	60.0
Textiles (knit)	0.32	2.2	0.44	0.12
Textiles (woven)	2.1	2.2	2.91	0.81

*All tons referred to in these reports are net tons, unless otherwise indicated.

**Approximate equivalent of 30 quads (1 quad is equal to 10^{15} Btu).

***Approximate equivalent of 37.5 quads.

****Approximate equivalent of 7.5 quads.

SECTION 2

FINDINGS AND R&D OVERVIEW

FINDINGS

So that the findings and general content of this report can be viewed in proper perspective, it is essential that the reader fully understand the purpose and scope of our study on "organic/toxic pollutants." Compared to the specific areas of air and water pollution control and solid waste disposal, the subject of "organic/toxic pollutants" is somewhat nebulous and, indeed, often requires a consideration of the several pathways by which pollutants enter the environment. In our original 13 industry studies, we examined, in conventional terms, the air pollution, water pollution, and solid waste disposal implications of energy-saving manufacturing process options. The subject of "organic/toxic pollutants" was not examined as a separate entity. Since the scope of this study largely restricts our data base to the original 13 industry studies, much of the material on "organic/toxic pollutants" had to be inferred from the nature of the air emissions, wastewater effluents, and solid waste streams from the various manufacturing processes. Since this study deals with a whole group of pollutants rather than a single pollutant or waste stream, and since many of these problems are only now being recognized, a quantitative comparison of organic/toxic pollutants would be next to impossible. Our treatment of the subject of organic/toxic pollutants is therefore qualitative. The main purpose of this report is to highlight those areas where the implementation of an energy-saving process option would result in a change in the quantity and/or composition of the organic/toxic pollutants discharged. Since specific identification of pollutants as "toxic" may be premature, we have used those materials identified in the June 1976 Consent Decree* as guidance.

Our findings regarding the implications of energy-saving manufacturing process options on the discharge of organic/toxic pollutants are presented below.

General Findings

- There is a wide variety of organic/toxic pollutants discharged from the base case manufacturing operations in the 13 industries studied. Where proper air and water pollution measures are

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*NRDC versus EPA, June 1976.

implemented, most of the identified organic/toxic pollutants are eventually discharged in the form of wet sludge or solid waste. However, since acceptable discharge levels to the environment are frequently not yet established, the acceptability of the final discharge is unknown.

- Many of the energy-saving process options have a negligible effect on the quantity and characteristics of the organic/toxic pollutants discharged when compared to conventional technology. This is not to be interpreted as no such pollutants are discharged but only that the change appears to be small.

- In those cases where there is an increase in the discharge of organic/toxic pollutants, the most prevalent cause is the conversion from natural gas or fuel oil to coal as the source of process energy. When using coal, the toxic pollutants generally of greatest concern are the large number of heavy metals contained in the coal, as well as polyaromatic organics.

Specific Findings

- Iron and Steel Industry - The base case manufacturing operations in the iron and steel industry generate organic/toxic pollutants that include phenol, cyanide, ammonia, sulfide, fluoride, and trace heavy metals. Substitution of dry quenching for wet quenching will tend to lessen discharge of organic and toxic pollutants. Otherwise, the new process options examined have very little effect on the discharge of organic/toxic pollutants.

- Petroleum Refining Industry - A variety of organic/toxic pollutants is found in the base case petroleum refinery discharges. These pollutants, including metal catalysts of polyaromatics, originate largely from the crude petroleum and its refined products.

  Most of the process options would result in very little change in the base case discharge of organic/toxic pollutants. In the Flexicoking process option, required air pollution control measures result in an additional small but concentrated wastewater stream that contains a variety of organic compounds, plus vanadium, which may require specific attention.

- Pulp and Paper Industry - While the base case processes in the pulp and paper industry generate large quantities of organic waste which is largely composed of wood-derived chemicals and degradation products and contains sulfur compounds, the waste as a whole is not generally considered toxic although numerous toxic compounds have been identified to be present in small amounts.

  Most of the process options either alleviate or have a negligible effect on the base pollution problem.

- Olefins Industry - The base case ethylene production unit discharges air, water, and solid waste streams that contain organic pollutants. The waste streams are not generally considered toxic.

  Both process options--naphtha cracking and gas oil cracking--will result in an increase in the quantity of organic pollutants discharged in the treated wastewater stream and in the solid waste streams. Due to the necessity for storing liquid hydrocarbon feedstocks, both process options will result in an increase in the amount of hydrocarbons that escape to the atmosphere, particularly as fugitive emissions. Whether these are or will be determined to be toxic is impossible to state without further study.

- Ammonia - The base case technology involving the production of ammonia from natural gas has very few environmental problems. There is a minimal discharge of organic pollutants.

  The process option based on the use of coal as a feedstock greatly increases the air, water, and solid waste pollution loads over the base case technology. Heavy metals present in both coal and slag--and which eventually appear in the treated wastewater and sludge streams--create a much more serious pollution problem than the waste streams from the base case technology. There is also a significant increase in the amount of organic pollutants appearing in the water and solid waste streams.

  The process option based on the gasification of fuel oil also results in a significant increase in the base case pollutional load, but to a lesser degree than the ammonia-from-coal process option.

- Alumina/Aluminum Industry

  Alumina - The base case Bayer process for the production of alumina from bauxite does not discharge organic pollutants. The disposal of very large quantities of "red mud," the insoluble residue that remains after alumina extraction, constitutes the chief environmental problem associated with alumina production. The red mud is highly alkaline and contains small quantities of heavy metals. However, they are in suspended form as hydroxides/oxides which are usually considered innocuous.

  Alumina production from domestic kaolin clays by the hydrochloric acid and nitric acid leaching processes produces even larger quantities of waste residues, which also contain heavy metals. The wastes from these two processes are acidic rather than alkaline and contain small amounts of organic reagents used in the processing; the metals will normally be in the less desirable soluble forms (chlorides, nitrates). The Toth alumina process, also intended for the extraction

of alumina from domestic clay, produces a waste similar to that generated by the hydrochloric acid process. Unless proper air pollution controls are used, it is possible for volatilized titanium and silicon tetrachlorides to be emitted to the atmosphere. Adjustments of pH to the basic side would appear to be a necessary treatment step for all three processes.

Aluminum - Aluminum production by the base case Hall-Heroult process discharges fluoride salts, hydrogen fluoride, and hydrogen sulfide to the atmosphere. Wet air pollution control systems transfer some of these pollutants to wastewater and, eventually, solid waste streams.

The Alcoa process eliminates the fluoride problem but, in its place, discharges considerable amounts of sodium chloride. If proper gas handling techniques are not employed, it is possible for chlorinated hydrocarbons to be discharged to the atmosphere. Carbon cathodes are used in the Alcoa process but are inert and thus, if implemented, would reduce emissions from the baking operation (prebaked or Soderberg cells) found in Hall-Heroult practice.

- Textile Industry - Dyes, dye carriers, phenols, formaldehyde, melamines, and the chromium compounds found in certain dyes are the major organic/toxic pollutants discharged by the base case processes in the textile industry.

  The process options mostly alleviate or do not alter the base case waste load, although the option based on a solvent (instead of aqueous) system has the potential for discharging significant amounts of perchlorethylene to the atmosphere, if that becomes the solvent of commercial systems, but could reduce discharge of organic/toxic finishing agents.

- Cement Industry - There is no discharge of organic pollutants and virtually no discharge of toxic pollutants (small amounts of heavy metals are sometimes present in cement dust) from the base case cement process.

  Of the process options considered, the only one that would introduce toxic pollutants into the waste streams is the option involving the conversion to coal fuel. Heavy metals are present in coal ash and can appear in waste cement dust. Depending on the ultimate use/disposal of these dusts, leaching may require some study. The storage and handling of coal also presents pollutional problems, which would be typical of any coal-using industry.

- Glass Industry - The base case natural gas-fired melting operation discharges air, water, and solid waste streams containing heavy metals originally present in the raw materials. The bulk of

the heavy metals is eventually discharged in the form of a solid waste stream from air cleaning.

The coal-based process options do not alter the emissions from the melting operation, but rather introduce additional emissions of heavy metals from the large quantities of coal ash produced.

- Chlor-Alkali Industry - The major discharge of organic/toxic pollutants from the base case diaphragm cell process is the solid waste from cell rebuilding that contains asbestos and lead, plus a waste stream from chlorine purification that consists of chlorinated organic compounds.

  The two process options, involving the use of dimensionally stable anodes and the use of modified diaphragms, both alleviate the organic/toxic pollutant problem by reducing the amount of asbestos discharged. The use of modified diaphragms virtually eliminates the chlorinated organic waste stream from the chlorine purification step.

- Phosphorus/Phosphoric Acid Industry - The base case process for producing high-grade phosphoric acid generates wastewater and solid waste streams that contain fluorides, phosphates, elemental phosphorus, and heavy metals.

  The process option involving the wet process production of phosphoric acid followed by chemical clean-up differs from the base case mainly in that large amounts of wet gypsum sludge are produced. The sludge contains fluorides, phosphates, and trace heavy metals, the latter as hydroxides/oxides.

  The solvent extraction clean-up process differs from the conventional process in that a large calcium chloride brine stream is substituted for a large fraction of the gypsum sludge and, consequently, heavy metals could be carried along as soluble chlorides. Pollutants associated with the base case (namely, fluorides, phosphorus, phosphates, and heavy metals) are still present, plus lost solvent consisting of normal butanol.

- Primary Copper Industry - There is no discharge of organic pollutants from the base case conventional smelting and refining process. Heavy metals (such as arsenic, antimony, bismuth, mercury, lead, zinc, and tellurium), mostly in the form of particulate matter, are present in air, water, and solid waste streams.

  From a pollutional standpoint, the pyrometallurgical process options do not represent a significant departure from the base case technology.

  The Arbiter process, however, has major pollutional implications. This hydrometallurgical process virtually eliminates the air

pollution problems associated with conventional smelting, but substantially increases the amount of solid waste destined for disposal. The solid waste is in the form of a wet sludge rather than a hard dry slag, and is therefore more prone to leaching of the heavy metals.

- Fertilizer Industry - There is no discharge of organic/toxic pollutants from the base case nitric acid plant or from the various process options intended for the control of NO_x emissions.

  The base case mixed fertilizer plant does not discharge organic/toxic pollutants. The process option involving the conversion from natural gas to fuel oil will likely result in wastewater and solid waste discharges containing phosphates, fluorides, and ammonia.

IDENTIFICATION OF CROSS-INDUSTRY TECHNOLOGY

As specifically related to the problem of organic/toxic pollutants, the only cross-industry, energy-conserving technology that has a significant impact on the nature and quantity of solid waste is the conversion from natural gas or fuel oil to coal. As noted earlier, these impacts would be very significant.

R&D AREAS

Since organic/toxic pollutants from many of the base case manufacturing operations and their process options are present in wastewater effluents, solid waste streams, and air emission, R&D activity pertinent to organic/toxic pollutants involves air pollution control, water pollution control, and solid waste disposal.

Air Pollution Control Technology

With regard to air emissions in the new technology investigated, we have identified the following to be deserving of R&D attention:

- Improving fine particulate removal technology. This would include especially those particulates resulting from metallic smokes and sublimed substances such as mercury, arsenic, zinc, etc. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with aluminum, ammonia, cement, copper, fertilizers, glass, iron and steel, petroleum refining, phosphorus, and pulp and paper.

- Collection or control of fugitive emissions from process equipment. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with aluminum, ammonia, copper, fertilizers, iron and steel, and textiles.

To a lesser extent, it is also a problem in the following industry sectors: cement, olefins, petroleum refining, phosphorus, and pulp and paper.

- Better definition of the environmental, health, and ecological impacts of gaseous emissions (such as SO_x, NO_x, CO, HF, Cl_2, NH_3) with respect to obtaining more quantitative knowledge for establishing bases for appropriate emission regulations. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with aluminum, ammonia, cement, chlor-alkali, copper, glass, iron and steel, petroleum refining, and pulp and paper.

  To a lesser extent, it is also a problem in the olefins industry.

- Better definition of the environmental, health, and ecological impacts of metallic smoke emissions with respect to obtaining more quantitative knowledge for the purpose of establishing the bases for appropriate emission regulations. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with aluminum, ammonia, cement, copper, glass, and iron and steel.

  To a lesser extent, it is also a problem in the olefins and petroleum refining industry sectors.

- Better definition of the environmental, ecological, and health impacts of organic compounds that have a high smog characteristic or potential carcinogenic properties. More quantitative knowledge is needed for the purpose of establishing bases for appropriate emission regulations. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with aluminum, iron and steel, olefins, petroleum refining, and textiles. To a lesser extent, it is also a problem in the pulp and paper industry.

- Improvements in odor control. Further information on the source of pollutants and nature of the problems (odor-causing pollutants) in new technology examined in this study is found in the Industry Assessment reports dealing with petroleum refining and pulp and paper. To a lesser extent, it is also a problem in the olefins industry.

- Improved instrumentation for rapid monitoring and recording of airborne emissions. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing

with aluminum, copper, glass, iron and steel, and pulp and paper. To a lesser extent, it is also a problem in the cement and petroleum refining industries.

Water Pollution Control Technology

With regard to water pollution control in new technology investigated in this study, we have identified the following as deserving consideration for additional research and development.

- Better definition of the environmental, health, and ecological impact of substances which cannot be removed by Best Available Technology Economically Achievable (BATEA). This would include principally metals and organic compounds that have long biological half-lives or carcinogenic effects. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with aluminum, ammonia, copper, iron and steel, petroleum refining, phosphorus, and pulp and paper.

- Removal of refractory organic compounds not achievable by technologies now designated by EPA as BATEA. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with iron and steel, textiles, petroleum refining, and olefins. To a lesser extent, it is also a problem in the aluminum industry.

- Improvements in suspended solids removal from treated wastewaters. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with ammonia, iron and steel, petroleum refining, phosphorus, and pulp and paper. To a lesser extent, it is also a problem in the aluminum, cement, chlor-alkali, and copper industry sectors.

- Improvements in color removal. Further information on the source of pollutants and nature of the color producing problems in new technology examined in this study is found in the Industry Assessment reports dealing with pulp and paper and textiles. To a lesser extent, it is also a problem in the petroleum refining industry.

- Removal of dissolved metals or inorganic salts. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with aluminum, iron and steel, and phosphorus. To a lesser extent, it is also a problem in the chlor-alkali, copper, glass, and petroleum refining industry sectors.

- Improved instrumentation for rapid monitoring and analysis of waterborne pollutants. This is really a pressing problem for all technologies in all industries. Further information on the specific source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with iron and steel and pulp and paper.

Solid Waste Disposal

With regard to solid wastes emanating from new technology investigated in this study, the following have been identified as deserving R&D attention:

- Demonstration of adequate landfill disposal techniques, including control of leachate. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with aluminum, cement, iron and steel, petroleum, refining, and phosphorus.

  To a lesser extent, it is also a problem in the ammonia, chlor-alkali, copper, glass, olefins, pulp and paper, and textile industry sectors.

- Demonstration of thermal destruction technologies. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with aluminum, olefins, and petroleum. To a lesser extent, it is also a problem in the chlor-alkali, iron and steel, and pulp and paper industry sectors.

- Additional research into the methods of categorization, regulation, and legal methodologies for controlling the disposal of solid wastes. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the Industry Assessment reports dealing with aluminum, ammonia, cement, copper, fertilizers, glass, iron and steel, olefins, petroleum refining, and phosphorus. To a lesser extent, it is also a problem in the chlor-alkali, pulp and paper, and textile industry sectors.

Thus, in each case, the direction of research programs should be viewed with the objective of attaining the maximum effectiveness for removing or controlling pollutants at the minimum economic penalty, since it is rarely possible to remove or control pollutants to present and anticipated standards without entailing cost penalties. Consequently, research programs must be examined within the framework of cost/benefits to the environment, to health, and to the economy.

SECTION 3

PROCESSES AND POTENTIAL TOXIC/ORGANIC DISCHARGES

BASES OF CALCULATIONS

In Volume III (page 19), describing the methodology used in this study, we indicate that selected State air emission regulations, along with the Federal Government's stationary source performance standards and effluent limitation guidelines, were surveyed to:

- establish the most probable limits of air and water emissions, and
- obtain a perspective of the types of pollution control systems to be considered.

While there are a large number of different regulations for airborne emissions at the State regulatory level, we found that approximately the same type of air pollution control systems would be required, regardless of the State or Federal regulations to be met. Generally, these air pollution control systems included baghouses, venturi scrubbers, and electrostatic precipitators for particulate and chemical-based systems for sulfur removal such as alkaline-based aqueous scrubbing for SO_x.

For water effluents we chose the EPA's Best Available Technology Economically Achievable (BATEA) guidelines (1983) as the effluent limitations that would have to be met for both currently practiced and the alternative processes considered. The rationale for this choice was that any plant employing the technologies evaluated in these reports should install wastewater treatment systems capable of meeting BATEA standards, although at the time of construction the New Source Performance Standards might be applicable. Because regulations for the handling and disposal of solid waste are either non-specific or non-existent, we chose various types of controlled landfill disposal methods, where our judgment suggested potential adverse environmental impacts might occur from uncontrolled disposal. At the time the original reports were prepared, the RCRA had not yet issued. It can only mean more stringent control will be needed by specific industries.

Potential toxic and organic compounds resulting from industrial processing (e.g., slags, fumes, slimes, and so on) and the suggested or expected treatment approach are described in the industry reports (Volumes III through XV) and are summarized in this section.

Recognizing that data are limited on process discharges, estimated waste loads after treatment become even more speculative. Keeping in mind that with nothing more than an approximation, we have generally assumed that treated waste loads are proportional to raw waste loads.

In the following sections, each industry is addressed in the order it was studied for the original study. Each base case technology is synopsized, including our information concerning the organic and toxic pollutants and their control. This is then followed by a parallel examination of the process option or options. It must be recognized, however, that for many of these options there is a dearth of reliable information, particularly in this nebulous area of "organics and toxics." As noted earlier, we have attempted to make judgments where these seemed appropriate.

IRON AND STEEL

The Basic Oxygen Process (BOP) for Steelmaking

Base Case Discharge of Organic/Toxic Pollutants--

The base case BOP unit (which is described in detail in Volume III, pages 18-28) is a complete combustion system in which the gases issuing from the mouth of the furnace are burned and collected in a hood, with considerable infiltration of air, and then cooled and cleaned of particulates before being released to the atmosphere.

Air Emissions and Wastewater Effluents - Most BOP units employ wet high energy scrubbers for dust collection. The dust consists mostly of iron oxide with small amounts of lime and/or calcium fluoride also present. If chromium-, lead-, or zinc-containing scrap is charged to the BOP, oxides of these metals may also be present in the dust. The dust-laden scrubber water is usually subjected to suspended solids removal in a sedimentation basin or clarifier. A portion of the water thus treated is recycled back to the scrubber, while the remaining water is discharged. The treated effluent water contains mostly suspended solids, sometimes with small amounts of dissolved fluoride and heavy metals present. Other than uncombusted carbonaceous particulate matter, few, if any, organic compounds are present in the gas and thus the wastewater stream.

Solid Waste - There are two significant solid waste streams associated with BOP operations--(1) slag and (2) wet sludge--resulting from dust collection.

Neither the composition nor the quantity of the slag is affected by the process changes selected for analysis in the original study; therefore, its disposal was not a subject of comparison in the study. The ultimate fate of BOP slag (as well as slag from other steelmaking processes) proceeds along three routes: (1) some of the slag is recycled to the blast furnaces; (2) some of it is sold to slag processors, where it is made into aggregate material for construction uses;

and (3) a portion is disposed of in landfills on or near the plant site. The slag contains iron and other metals present in the scrap charged to the furnace as well as calcium fluoride, all in a solid matrix. Smaller (trace) amounts of other metals may also be present.

The wet sludge resulting from dust collection is removed from the sedimentation basin and usually subjected to mechanical dewatering to further reduce its volume prior to reclamation of iron values and/or disposal. The ability to reclaim iron values depends upon the composition of the dust, which is influenced by the nature of the scrap charged to the BOP. If clean uncoated home scrap is used, the dust consists primarily of iron oxides and can be recycled to the sinter strand. If purchased scrap is used, it may not be possible to control the composition closely; as a result, the dust and resultant sludge can contain lead, zinc, tin, and other metals, thereby reducing the potential for recycle. Such sludge is usually disposed of to landfill.

BOP Off-Gas Recovery--

When off-gas recovery is incorporated into a BOP unit, the carbon monoxide containing off-gas may be collected for eventual use as an internal plant fuel, rather than allowed to combust naturally as in the conventional BOP (see Volume III, pages 18-23).

BOP units equipped with off-gas recovery produce lower gas volumes than conventional BOP units, due to the marked reduction in the volume of infiltration air. Gas-cleaning equipment in both cases consists of high-energy venturi scrubbers. The quantity of dust is essentially the same for conventional and off-gas recovery-equipped BOP units. The composition of the dust, however, is slightly different. In the conventional BOP operation where the carbon monoxide is burned with entrained air, the dust particles are largely oxidized. In BOP units equipped with off-gas recovery, the dust is subjected to far less oxidation and, therefore, contains a higher fraction of unoxidized or partially oxidized species. A comparison of the dust compositions is presented in Volume III, page 25.

The Conventional Blast Furnace for the Production of Iron

Base Case Discharge of Organic/Toxic Pollutants--

The base case process is the conventional blast furnace used in the production of iron. Iron ore, coke, limestone, and fluorspar are charged to the furnace which is operated under reducing conditions to convert the iron oxide to the metallic iron. The operation of the blast furnace results in wastewater effluents,solid wastes, and air emissions (see Volume III, pages 64-78, for description).

Wastewater Effluents - Blast furnaces are equipped with air pollution control systems that employ wet scrubbers for the removal of particulate matter. The scrubber water is subjected to gravity settling.

Part of the effluent from the gravity settling step is recycled to the scrubbers, while the remainder is discharged. The wastewater effluent contains suspended solids, phenol, cyanide, sulfide, ammonia, fluoride, and certain heavy metals. Future water pollution regulations will require that the wastewater be subjected to further treatment steps for the removal of large portions of many of the above pollutants.

Solid Waste - A blast furnace produces two major solid waste streams: (1) wastewater treatment sludge and (2) slag.

- Wastewater Treatment Sludge - The particulate matter originally present in the blast furnace gas is removed from the scrubber water stream as a wet sludge. While the solid phase of the sludge is relatively innocuous (containing mostly carbon and iron particulates), the liquid fraction is similar to the above-described wastewater stream, containing phenol, cyanide, sulfide, ammonia, fluoride, and certain heavy metals. A portion of the dewatered wastewater treatment sludge is usually recycled back into the process for reclamation of iron values.

- Slag - A large fraction of the slag generated by blast furnaces is sent to slag processors where it is converted into aggregate material for construction. When the demand for the slag is less than the supply, the excess slag must be disposed of on land. Blast furnace slag generally contains small quantities of heavy metals such as chromium, copper, manganese, nickel, lead, and zinc, as well as fluoride. The materials in the slag are fused together in a relatively inert solid matrix; under normal conditions, they are not prone to leaching.

Air Emissions - We do not believe that air emissions from blast furnaces will be noticeably affected by implementation of external desulfurization.

External Desulfurization --

Coke, containing some of the sulfur found in the coal used, is the major contributor to the total amount of sulfur entering the blast furnace. Other sources of sulfur in the blast furnace include fuel injections, the scrap mixed with the burden, and the minerals themselves (ore, limestone).

Only a small portion of the sulfur is found in the off-gases; most of the sulfur leaving the blast furnace appears in the liquid slag and hot metal. The capacity of the slag to retain sulfur is generally increased as more limestone is added. Limestone, however, increases coke consumption, which in turn introduces more sulfur. Clearly, then, there is a limit to the amount to which this "internal" desulfurization is viable. It may be advantageous to tap a hot metal containing more sulfur than specified, and to add to the process sequence a new step: the injection of desulfurization agents into the molten iron during its transfer from the blast furnace to the steelmaking furnace. These agents (usually calcium compounds) react with the dissolved sulfur and form a sulfide slag that can be disposed of. This additional step is called external desulfurization.

External desulfurization can provide two energy-related benefits: (1) it can reduce coke consumption, and (2) more importantly, it decreases the dependence on low-sulfur metallurgical coal, which is becoming increasingly difficult to obtain.

The external desulfurization process produces a gaseous emission which contains particulates and possibly some cyanide (the process takes place under reducing conditions; other organic compounds may possibly be present). If the gas stream is subjected to wet scrubbing, a wastewater stream will be produced which will be not unlike that of the parent blast furnace. If the wastewater is treated in the same manner as blast furnace wastewater, a similar type of wet sludge will be produced. The additional wastewater treatment sludge stream from the external desulfurization step must be balanced against the reduced volume of blast furnace gas and the sludge that results from cleaning it.

The external desulfurization process reduces the amount of coke and limestone used in the blast furnace, thereby reducing the amount of slag generated in the blast furnace proper. While external desulfurization produces a slag stream of its own, the overall effect is a net reduction in the amount of slag generated. It appears that the external desulfurization process will not appreciably alter the overall discharge of pollutants from the base case blast furnace.

The Quenching Operation in Coke-Making

Base Case Discharge of Organic/Toxic Pollutants--

Current technology involves wet quenching of coke as described in Volume III, page 48. In wet quenching, hot coke (at 1900-2000°F) is delivered in a coke car to a tower where the coke is quenched with water, thereby producing large quantities of steam which are vented to the atmosphere. The coke car is designed to allow the excess water to drain. This water is usually recirculated, thereby eliminating wastewater discharge.

If contaminated wastewater is used for coke quenching, air pollution can result when organic contaminants in the wastewater are volatilized into the air/steam plume that evolves during the quenching. The use of clean water minimizes the emission of objectionable organic vapors, and the installation of baffles in the quench tower is claimed to remove solid particles satisfactorily (Volume III, page 48). However, at this time, there are no regulations requiring use of clean water.

Dry Quenching of Coke--

In the dry quenching of coke, the hot coke pushed from the ovens is cooled in a closed system, as described in Volume III, page 48. Dry quenching uses inert gases to extract heat from incandescent coke by direct contact. The heat is then recovered in a waste heat boiler or by other techniques. The inert gases can be generated from an initial intake of air which reacts with the hot coke to form a quenching gas largely composed of nitrogen, carbon dioxide, and carbon monoxide.

The dry quenching process eliminates the type of emissions that are normally associated with wet quenching; however, there are still a number of particulate emissions which must be controlled. While the amount of emissions are largely based on the system design and no actual data are available, it appears that the dry quenching process has a greater potential for reducing air pollution than the wet quenching process and, in so doing, would lessen the discharge of any organic or toxic pollutants.

Conventional Iron and Steelmaking Base Case for Comparison in the Direct Reduction of Iron Ore

Base Case Discharge of Organic/Toxic Pollutants--

Direct reduction of iron ore is designed to replace the blast furnace along with its supporting coke plant. In the version of the direct reduction process selected for comparison (coal-based rotary kiln; see Volume III, page 59), the reduced product iron from the direct reduction unit is sent to an electric arc furnace (rather than a more conventional open hearth or basic oxygen process furnace) for steelmaking. In order to compare direct reduction with the existing technology on an equivalent basis, it is necessary to make the comparison all the way through the steelmaking process. Thus, the base case process consists of the following units:

- Byproduct coke plant,
- Blast furnace, and
- BOP furnace.

A variety of wastewater effluents, solid waste streams, and air emissions are generated by the base case group of processes:

Wastewater - Pollutants of concern in coke plant wastewater are phenol, ammonia, cyanide, sulfide, oil and grease, and a number of other organic and sulfur compounds.

Blast furnace wastewater also contains the above pollutants in addition to fluoride and heavy metals. Even after the application of the recommended treatment steps, measurable amounts of these pollutants are present in the treated wastewater.

Wastewater from the basic oxygen process contains mostly suspended solids and a small amount of fluoride.

Solid Waste - The major solid waste streams from the base case process operations are described below:

- Byproduct Coke - Solid waste includes coke dust and wastewater treatment sludge. The water fraction of the sludge can contain phenol, oil and grease, cyanide, ammonia, sulfide and other organic and sulfur compounds, many of which can be considered as toxics.

- Blast Furnace - Solid waste includes slag and wastewater treatment sludge. The slag is generally sold to a slag processor for conversion into construction material. The liquid fraction of the wastewater treatment sludge can contain phenol, ammonia, cyanide, sulfide, fluoride, and heavy metals. Much of the sludge is recycled back into the process for the reclamation of iron values.

- Basic Oxygen Furnace - Solid waste includes slag and wastewater treatment sludge. BOP slag is also reprocessed, and the wastewater treatment sludge (containing mostly particulates, iron oxides, and fluoride) is usually recycled.

Air Emissions - The base case group of processes produces air emissions consisting mostly of particulate matter composed of carbon, iron oxide, and a small amount of calcium fluoride.

Direct Reduction--

The direct reduction process is described in detail in Volume III, pages 54-87. In the direct reduction process, iron oxides, coal, and lime for desulfurization are mixed and charged into a rotary kiln. Coal provides the reducing gas (carbon monoxide) and the heat for the reduction of iron oxides. Air is admitted at the lower end of the kiln and along the length of the kiln. After the reduction has taken place, the products pass into a cooling drum where they are cooled to prevent reoxidation. The cooler discharge, consisting of sponge iron, excess coal, coal ash, and desulfurizing agents, is split into the individual components by screening and magnetic separation. The excess coal is largely recycled.

There is one significant wastewater stream from the direct reduction process: the kiln exhaust gas scrubber water. The exact composition of the exhaust gas is not known; however, the exhaust gas and its associated scrubber water should be similar to those of the conventional blast furnace, and would therefore very likely contain suspended solids, phenol, cyanide, ammonia, and sulfide. Since no fluorspar fluxing agent is used in the direct reduction process, there would not be any fluoride in the scrubber water.

The sludge from the wastewater treatment system is expected to be similar to blast furnace sludge in that the liquid fraction of the sludge would probably contain cyanide, ammonia, phenol, and sulfide.

Instead of producing slag, as in the case of the conventional blast furnace, the direct reduction process produces coal ash and a residue consisting of the spent desulfurization agents. The electric furnace that converts the product iron from the direct reduction step into steel produces a slag and air pollution control dust.

Air emissions are mostly particulates.

Overall, we do not expect that the direct reduction process option will increase the discharge of organic/toxic pollutants, and, in fact, it should alleviate some of the pollution problems associated with the base case process, mainly due to the elimination of the coke oven. However, these changes will, with the exception of CaF_2, be in amounts rather than in character.

Summary

The base case basic oxygen process for steelmaking discharges mostly solid matter to the environment, in wastewater effluents, solid waste streams, and air emissions. The particulates mainly consist of carbon and iron oxide particles, with a small amount of calcium fluoride and heavy metals also present. The process option for the basic oxygen process is off-gas recovery, which has only a very minor effect on the nature of the pollutants discharged.

The conventional blast furnace discharges a variety of pollutants which are mostly in the form of wastewater effluents and solid waste streams. The pollutants of greatest concern are phenol, cyanide, sulfide, ammonia, fluoride, and heavy metals. While the external desulfurization process option results in a net reduction in the overall amount of slag produced, its incorporation into a conventional blast furnace operation is not expected to appreciably alter the nature or quantity of the overall discharge of pollutants.

Dry quenching of coke has at least the potential for generating a smaller amount of air emissions than the base case wet quenching process, and, of course, eliminates the water pollution inherent in wet quenching.

The overall conventional steelmaking process, including the basic oxygen furnace, the blast furnace that supplies the iron, and its supporting coke plant discharges pollutants as wastewater effluents, solid waste streams, and air emissions. The pollutants of concern are phenol, cyanide, ammonia, sulfide, oil and grease, fluoride, and heavy metals. The direct reduction process option eliminates the coke plant, substitutes the blast furnace with a direct reduction kiln, and replaces the basic oxygen furnace with an electric furnace. Since fluorspar fluxing agent is not used in the direct reduction process option, fluoride will not be present in the effluent. Mainly due to the elimination of the coke oven, the direct reduction process should result in at least a slight decrease in the base case pollutional load. Of course, the electric arc furnace must be considered to generate the typical airborne, waterborne, and solid wastes at the power plant, either on-site or at the utility, during generation of the required electricity. Whether these wastes, after treatment by existing technology, are harmful is an unresolved point.

PETROLEUM REFINING

The Total Petroleum Refining Process

Base Case Discharge of Organic/Toxic Pollutants--

For the purpose of performing economic and energy utilization comparisons, three base case refineries have been established--an East Coast refinery, a West Coast refinery, and a Gulf Coast refinery. The base case refineries reflect differences in feedstock, process configuration, and product mix. A detailed description of the process technology and energy consumption patterns embodied by the three base case refineries is presented in Volume IV, pages 111-133.

From an environmental point of view, there is very little difference between the three base case refineries. The treated wastewater effluent pollutant loadings and the rates of solid waste generation are estimated to be the same for all three refineries. There is only a slight difference between the three refineries in the magnitude of the air emissions. A variety of organic (and possibly toxic) pollutants are present in the air emissions, wastewater effluents, and solid waste streams from refineries. In terms of the type of pollutants present, there is virtually no difference between the three base case refineries.

Wastewater - The major refinery wastewater streams are process water, cooling tower blowdown, and boiler blowdown. Many of the organic constituents found in petroleum appear in the wastewater for the simple reason that there is contact between water and petroleum products during processing. Constituents present in the process wastewater include free oil, dissolved hydrocarbons, sulfur and nitrogen compounds (such as sulfides and ammonia), coke, and inorganic particulates. As a result, process wastewater exerts both a chemical (COD) and a biochemical oxygen demand. The presence of phenols and aromatic hydrocarbons is of particular concern. The process wastewater is usually subjected to biological treatment and physicochemical separation processes to remove a large percentage of the organic matter prior to discharge. The cooling tower blowdown often contains chromium compounds which are used as corrosion inhibitors.

Solid Waste - A petroleum refinery generates a wide variety of solid wastes, many of which contain petroleum-derived organic compounds identified as toxic substances (NRDC, 1976). Basically, refinery solid waste streams fall into two main groups: those that are intermittently generated and those that are continuously generated.

The intermittent wastes are generally those that result from cleaning within the process areas and off-site facilities of the refinery. The following are typical intermittent waste streams:

- Process vessel sludges, vessel scale, and other deposits generally removed during plant turnarounds;
- Storage tank sediments; and
- Product treatment wastes, such as spent filter clay and spent catalysts from certain processing units.

Continuous wastes (those requiring disposal at less than two-week intervals) can be further broken down into two groups: process unit wastes and wastewater treatment wastes.

Major process unit wastes include:

- Coker wastes, such as coke fines from delayed or fluidized cokers, and spilled coke from unloading facilities;
- Spent catalysts and catalyst fines from the fluid catalytic cracking units; and
- Spent and spilled grease and wax wastes from lube oil processing plants.

Wastewater treatment wastes can include:

- Waste biological sludges from activated sludge units; and
- Dissolved air flotation float.

Typically such wastes are dewatered by means of sludge thickeners, coupled with vacuum filters or centrifuges. The dewater sludge can then either be land-disposed or incinerated. Low concentrations of heavy metals are usually present in the sludges.

A summary description of major refining solid waste streams is presented in Table 14 (Volume IV, page 160).

Air Emissions - Petroleum refineries emit significant quantities of pollutants to the atmosphere. In addition to particulates, sulfur dioxide, and nitrogen oxides, there are also relatively large emissions of organic vapors, including aldehydes and hydrocarbons.

Process Option A-1 - Direct Combustion of Asphalt in Process Heaters--

Presently, the asphalt fraction of a refinery's output is usually subjected to several processing steps to make it suitable for sale as a construction material. Asphalt has characteristically been a very low value refinery product. As a result, the processing and sale of asphalt are more of a "least cost" means of disposal rather than an important source of revenue.

Internal refinery heat energy requirements are supplied by combusting portions of the refinery output. By introducing asphalt into the total refinery heat generation system, a greater quantity of higher value fuels is made available to the consumer. Thus, while the direct combustion of asphalt does not save energy in an absolute sense, it does improve the overall form value of the refinery product mix. Direct combustion of asphalt is considered to be most feasible for the base case East Coast refinery.

Wastewater - It is anticipated that an East Coast refinery employing direct combustion of asphalt will have a treated process wastewater effluent and a treated cooling tower blowdown that will be of the same volume and composition as that of the base case East Coast refinery.

Solid Waste - Implementation of direct combustion of asphalt will not appreciably alter the quantity or characteristics of the base case East Coast refinery total solid waste stream.

Air Emissions - Asphalt contains an appreciable amount of sulfur and ash. The direct combustion of asphalt will result in a significant increase in the amount of sulfur dioxide emitted. Flue gas desulfurization would be required and would convert the sulfur that is removed from the gas stream into a sulfuric acid byproduct. It is not clear whether the direct combustion of asphalt would have any effect on the base case emission of hydrocarbons.

Process Option A-2 - Hydrocracking of Heavy Bottoms--

The purpose of this process is to convert heavy ends into lighter, more usable fuels. As in the case of direct combustion of asphalt, it is designed to improve the form value of the refinery product mix rather than to conserve energy in absolute terms. It is intended for use in a West Coast base case refinery.

Wastewater - It is anticipated that a West Coast refinery employing heavy-bottoms hydrocracking will have essentially the same wastewater volume and characteristics as the base case West Coast refinery. The only incremental (over the base case) waste load is a small sour water (sulfide-containing) stream which increases the total process wastewater flow rate by only 0.25%.

Solid Waste - Implementation of heavy-bottoms hydrocracking will slightly alter the total quantity of refinery solid waste. This process will require the disposal of a chrome-molybdenum catalyst which will slightly increase the base case quantity of solid waste disposal.

Air Emissions - Due to the sulfur content of heavy bottoms, there will be an increase in hydrogen sulfide and sulfur dioxide emissions which will have to be controlled by using an amine scrubber and a

Claus plant. It is not clear whether the hydrocracking of heavy bottoms would have any effect on the base case emission of hydrocarbons.

Process Option A - Flexicoking--

The Flexicoking process is most applicable to East Coast refineries. Flexicoking is the combination of fluid coking with coke gasification; it contributes to energy conservation in two ways: (1) it frees high-Btu refinery gas for higher priority uses, and (2) it converts asphalt feed to naphtha and gas oil intermediates which then become available for refining. This represents a portion of crude which otherwise would not be a salable fuel product.

Wastewater - It is anticipated that an East Coast refinery employing Flexicoking will have a treated process wastewater stream very nearly the same as that of the base case East Coast refinery. The total volume of waste load will be slightly increased due to the presence of additional sour water and increased cooling tower blowdown.

The use of Flexicoking increases the amount of sulfur that must be removed from gaseous streams. The sulfur in the high-Btu fuel gas is removed using an amine scrubbing system, and the exhaust from that scrubbing system is sent to the refinery gas plant. The hydrogen sulfide in the low-Btu "flexigas" is too low in concentration to be economically scrubbed out, and, therefore, this process comes with an integral Stretford unit for sulfur removal. The Stretford unit has a liquid purge stream which contains rather high concentrations of metallic and organic compounds. A typical composition of a Stretford purge stream is shown below.

TYPICAL COMPOSITION OF STRETFORD PURGE SOLUTION

Constituent	mg/l
Na_2CO_3	4,700
Sodium Anthraquinone Disulfonate	700
$NaVO_3$ (sodium meta-vanadate)	300
Sodium Citrate	300
$Na_2S_2O_3$	6,000
Na_2SCN	6,000

Source: "Characterization of Sulfur Recovery from Refinery Fuel Gas," U.S. Environmental Protection Agency, EPA-450/3-74-055, p. 36.

The disposal of Stretford purge solution presents a problem. It contains compounds that could disrupt the performance of a biological wastewater treatment system should it be discharged to the main refinery wastewater system. First, it may have to be concentrated and then disposed of in a lined disposal site, much in the manner of a solid waste stream.

Solid Waste - In addition to the base case solid waste load, the Flexicoking process will also produce a solid waste stream consisting of coke fines that will more than double the base case solid waste generation rate. The coke fines, however, are not considered particularly objectionable in terms of potential environmental problems.

Air Emissions - As discussed under the section on water pollution, increased sulfur emissions are the major increase in the base case level of air emissions. It is not clear whether the implementation of Flexicoking would have any effect on the base case emissions of hydrocarbons.

Process Option B - On-Site Electric Power by Combustion of Vacuum Bottoms--

In this process option, electric power is generated internally within the refinery rather than purchased from the local power utility. The internal generation of electric power within the refinery does not conserve energy overall--nor does it consume more energy than when power is purchased, assuming that the internal and external power plants would operate at the same efficiencies. In effect, the form value of the asphalt product is upgraded to a higher form of electric power for refinery use. This process option is most applicable to the base case Gulf Coast refinery.

Wastewater - The only water pollutional implications of a Gulf Coast refinery employing on-site power generation via asphalt combustion will be increased cooling tower and boiler blowdown flow rates. The process wastewater flow rate and composition will be essentially the same as the base case.

Solid Waste - The total solid waste stream for on-site power generation is essentially of the same volume and composition as that of the base case.

Air Emissions - The major pollutant of concern is the sulfur dioxide emission in the exhaust from the boiler. The emission of hydrocarbons will be essentially the same as the base case Gulf Coast refinery.

One must also recognize that off-site electricity generation would also produce pollutants, the nature of which will be dependent on the fuel used by the utility.

Process Option C - High Purity Hydrogen Production via Partial Oxidation of Asphalt--

This alternative is based on the production of high-purity hydrogen for hydrotreating from vacuum bottoms, using a partial oxidation process. The feedstocks freed up by this approach would then be available for sale outside the refinery in the form of pipeline gas or naphtha. This alternative is considered most applicable to a West Coast base case refinery.

Wastewater - It is anticipated that a West Coast refinery employing hydrogen production via partial oxidation will have a treated process wastewater effluent and a treated cooling water blowdown stream that will be slightly greater than that of the base case West Coast refinery and similar in composition.

Solid Waste - Implementation of hydrogen production via partial oxidation at the base case West Coast refinery will slightly increase the volume of the total solid waste stream due to the slightly increased quantity of wastewater treatment sludge. In addition there will be a small waste catalyst stream containing iron, chromium, copper,and zinc, which are often landfilled.

Air Emissions - Increased sulfur emissions are the only change in the base case air pollution profile.

Summary

Wastewater effluents, solid waste streams, and air emissions from petroleum refineries contain a variety of organic (and sometimes toxic) pollutants that originate largely from the petroleum and its products processed within the refinery.

The treated wastewater effluent streams of the base case refinery would not be significantly altered by the implementation of the process options. The most significant impact on wastewater would result from the Flexicoking process option which produces an additional wastewater stream that is small in volume and contains high concentrations of organic compounds as well as vanadium.

Most of the process options result in increased sulfur dioxide emissions; however, we do not expect the base case hydrocarbon emissions to be significantly increased by any of the process options.

Hydrocracking of heavy bottoms adds a small chrome-molybdenum catalyst stream to the base case solid waste discharge; Flexicoking adds large quantities of relatively inert coke fines; and the partial oxidation process option adds to the base case a small catalyst stream that contains iron, chromium, copper, and zinc.

A qualitative comparison of organic/toxic pollutant discharges is presented in Table 2. In the final analysis, it does not appear that new organic or toxic pollutants from the several proposed process options will influence the decisions on implementation of these processes.

PULP AND PAPER

Bleached Kraft Pulping

Base Case Discharge of Organic/Toxic Pollutants--

A detailed description of the base case Kraft process is given in Volume V, pages 54-60. Mills employing the conventional process steps for producing bleached Kraft pulp discharge organic pollutants into the air, water, and solid waste streams. The organic material originates from the wood itself. (Although pentachlorophenol was formerly used by many mills to inhibit microbial degradation in wood storage piles, the industry has largely eliminated this practice specifically because of concern over the discharge of this substance to the environment.) In the manufacture of bleached Kraft pulp, a certain fraction of the wood undergoes a variety of complex reactions with the caustic soda/sodium sulfide cooking liquor and the chlorine or chlorine-based chemicals used in the bleaching step. The result is a wide array of complex organic species in the wastes.

Both soluble and insoluble components of the original wood and the reaction byproducts are discharged as aqueous effluents. When chlorine bleaching is used, the reaction between the chlorine and chemicals in the wood may result in the formation of chlorinated organic compounds, such as chlorophenols. Wood hydrolysis products are also present. Typically, the various wastewater streams are combined into a single stream and treated in a central wastewater treatment plant. As in most industries, pulp and paper mill wastewater effluents are usually characterized by gross parameters, such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, and color, rather than by the identification of specific compounds. The wastewater is usually subjected to suspended solids removal followed by biological treatment for the removal of biodegradable organic matter. Treated Kraft mill effluents, although still containing significant amounts of BOD, COD, and color, are not considered toxic, even though numerous "toxic" components have been identified as present, at least in small amounts.

The wastewater treatment plant produces a wet sludge which is composed largely of wood fibers, inorganic particulate matter, and excess micro-organisms from the biological treatment step. The sludge is usually subjected to mechanical dewatering to reduce its volume prior to land disposal on or near the plant site. The sludge is not considered toxic. As with many other organic sludges, both inorganic and organic sulfur compounds present in both the liquid and solid phases of the sludge can be partially converted to offensive hydrogen sulfide gas by microbial activity if the sludge is subjected to anaerobic conditions.

TABLE 2. PETROLEUM REFINING INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
Base case petroleum refinery	Petroleum-derived organic compounds, sulfide, and ammonia in treated effluent.	Emission of organic vapors (including aldehydes) to the atmosphere.	Petroleum containing process and wastewater treatment sludges. Small amounts of heavy metals present.
Process option A-1: direct combustion of asphalt	Same as base case.	Increased SO_x emissions but organic pollutants expected to be similar to base case.	Same as base case.
Process option A-2: hydrocracking of heavy bottoms	Very slight increase over base case in quantity; character very similar.	Increased SO_x emission but organic pollutants expected to be similar to base case.	Base case solid waste discharge plus discharge of a chrome-moly catalyst.
Process option A-3: flexicoking	Base case waste load plus small wastewater stream containing organics and vanadium.	Increased SO_x emissions but organic pollutants expected to be similar to base case.	Base case solid waste discharge plus major addition to solid waste load due to coke fines.
Process option B: On-site electric power by combustion of vacuum bottoms	Base case waste load plus slight increase in cooling tower blowdown and boiler blowdown.	Increased SO_x emissions but organic pollutants expected to be similar to base case.	Same as base case.
Process option C: High-purity hydrogen production via partial oxidation of asphalt	Slight increase in base case waste load.	Increased SO_x emissions but organic pollutants expected to be similar to base case.	Slight increase in base case waste load. Additional small catalyst stream containing iron, chromium, copper, and zinc.

Air emissions from a conventional Kraft mill contain small (yet odoriferous) amounts of hydrogen sulfide and organic sulfur compounds, such as methyl mercaptan and dimethyl sulfide. Through both process modifications and improved operational controls, the magnitude of these emissions has been greatly reduced in recent years.

Process Option 1 - Alkaline-Oxygen (A-O) Pulping--

A process description of alkaline-oxygen pulping is provided in Volume V, pages 84-85. In terms of pollution control considerations, its most significant feature is that it employs a non-sulfur cooking step that would eliminate the air pollution from malodorous sulfur compounds and greatly alleviate the bleach plant liquid effluent problem.

It is expected that the wastewater effluent flow rate will not be significantly changed as a result of A-O pulping. However, elimination of two of the standard bleach stages should result in approximately a 50% reduction in both raw wastewater BOD and color for A-O compared with Kraft. If the wastewater is treated by the same means in both cases, i.e., by biological methods, the quantity of BOD and color in the treated effluent will also be lower for A-O pulping. In addition, the quantity of sulfur compounds in the treated effluent will be greatly reduced, being the result only of the sulfur originally present in the wood.

Since the quantity of sludge produced by a biological treatment system is proportional to the amount of BOD removed, a reduction in the total raw waste load BOD will reduce the quantity of the biological fraction of the wastewater treatment sludge. The sludge will contain a far smaller quantity of sulfur compounds.

By eliminating malodorous sulfur compounds, the implementation of A-O pulping will have a beneficial effect on air pollution control. In addition to the virtual elimination of organic sulfur compounds (measured as total reduced sulfur), A-O pulping is expected to result in a slightly lower level of particulate emission (Volume V, page 9).

Process Option 2 - The Rapson Effluent-Free Kraft Process--

The Rapson effluent-free Kraft process is described in Volume V, pages 95-97. It essentially consists of a number of modifications to the conventional Kraft process which are designed to increase the amount of chemical recovery and water recycle. As its name implies, the main environmental advantage of the Rapson process over conventional Kraft processes is the elimination of water effluent from the bleaching step.

A mill using the Rapson process would produce significantly less wastewater than a conventional bleached Kraft pulp mill. Thus, for the application of a given type of wastewater treatment, the Rapson process would discharge less organic pollutants in the treatment wastewater effluent. The type of pollutants would be very nearly the same as those associated with the conventional Kraft process.

Since the wastewater flow rate and the quantity of pollutants in the wastewater are lower for the Rapson process as compared to the conventional Kraft process, it is anticipated that the quantity of wastewater treatment sludge would also be less. There is, however, a small stream of salt cake (sodium sulfate) leaving the process which can either be disposed of or sold.

Air emissions from the Rapson process are expected to be essentially the same, both in terms of composition and magnitude, as the air emissions from the conventional Kraft process.

Mechanical Pulping

Base Case Discharge of Organic/Toxic Pollutants--

Mechanical pulping processes are described in Volume 5, pages 98, 105-113. Mechanical pulp (i.e., wood reduced to fiber by grinding) is typically combined with wood fiber produced by chemical means and used primarily in the manufacture of newsprint. It is also used in combination with chemical fiber in the manufacture of catalogue paper, construction paper, and other so-called groundwood papers. Wood chips, sawdust, and shavings from saw mills can be used as raw material.

Since no chemicals are used in mechanical pulping, the organic materials present in the wastewater stream are those present in the wood itself and its hydrolysis products. The wood-derived organic material is present as both wood fiber and as dissolved chemical species. The quantity of color and sulfur compounds are less than in Kraft mill effluent since the only sulfur present in mechanical pulping would be that contained in the wood. The wastewater is subjected to suspended solids removal and biological treatment for the removal of biodegradable organic matter.

Solid waste from mechanical pulping is mostly wastewater treatment plant sludge similar to that produced by Kraft mill wastewater treatment facilities. The sludge will, however, contain a far smaller amount of organic sulfur compound.

Air emissions are not generally a serious problem for mechanical pulping operations. There is virtually no emission of organic sulfur compounds, as in the case of Kraft mills. The only organic materials discharged to the air are small quantities of fine particulate wood fiber from the wood preparation steps.

Process Option - Thermo-Mechanical Pulping (TMP)--

In the TMP process, described in detail in Volume V, pages 98, 105-113, the wood is preheated to 266°F (130°C) for a short period and then reduced to fibers in a pressurized device. The incentive to switch to TMP has been the improved fiber properties and resultant expansion of the wood

source base, i.e., the ability to use chips and residual wood to a greater degree than if conventional mechanical pulping were employed.

The elevated temperature of the TMP process causes slightly more organic matter to dissolve from the wood and eventually appear in the wastewater effluent as an additional BOD loading. Thus, for a given type of wastewater treatment applied, the implementation of the TMP process will slightly increase the amount of organic material discharged to the aquatic environment. However, the composition is expected to be essentially unchanged.

Since the amount of sludge produced is proportional to the amount of pollutants removed, TMP will also result in a slight increase in the quantity of wastewater treatment sludge generated. The nature is expected to be very similar.

No significant difference between the air emissions produced by the TMP process and the base case mechanical pulping process is expected.

The Manufacture of Newsprint

Base Case Discharge of Organic/Toxic Pollutants--

Newsprint is manufactured from blends of mechanical pulp and Kraft pulp (described in Volume V, pages 113-119). The discharges associated with these processes have been discussed in the preceding sections. Other than a minimal contribution from those pollutants retained by the pulp (particularly the Kraft), pollution would be restricted to non-toxic surfactants, wetting agents, etc., used in the paper-making.

Process Option - The De-inking of Old News for Newsprint Manufacture--

The de-inking of old news for newsprint manufacture is a well-established commercial process which is described in detail in Volume V, pages 113-119. Although the concept of blending recycled fiber with virgin mechanical fiber is not new, it has only recently been introduced for the manufacture of newsprint on a large scale. It was chosen for in-depth technical/economic analysis because the production of newsprint containing de-inked news now accounts for less than 5% of the total newsprint consumed in the United States and its broader application could significantly reduce both energy usage and pollution.

De-inking is carried out by washing and pulping the old news in either a batch or continuous operation using heat, water, and de-inking chemicals, typically consisting of sodium peroxide, sodium silicate, and detergents. The de-inking chemicals are largely recoverable.

The de-inking operation produces a wastewater that is quite high in suspended solids, composed largely of unrecovered fibers from the paper itself. The wastewater will also contain ink particles and the chemicals

contained within the ink. Letterpress newsprint ink is made of carbon black particles suspended in a mineral oil vehicle that may also contain rosin and other additives. Litho newsprint ink (used for color printing in magazines) is composed of various dye materials suspended in a vehicle which may contain resins dissolved in aliphatic hydrocarbon solvents. Thus, the wastewater may contain not only natural organic material from the wood itself, but also small quantities of synthetic and petroleum-based hydrocarbons. Although the wastewater contains higher levels of suspended solids than the wastewater from the various mixes of mechanical pulp and Kraft pulp that constitutes the base case, the concentration of BOD is very nearly the same, if not slightly lower.

The de-inking operation produces a wet waste sludge consisting of paper or cellulose fiber and ink particles which is usually sent to landfill.

Also, de-inking operations produce slightly more wastewater treatment sludge than the base case. Although it is difficult to quantify, it is clear that, overall, the implementation of de-inking of old newsprint will alleviate the national solid waste disposal problem by substantially reducing the amount of old news destined for municipal landfills.

There are no significant air emissions of organic materials from the de-inking of news for newsprint.

Summary

The base case conventional bleached Kraft pulping process discharges wood-derived organic material into air, water, and solid waste streams. The two options to the conventional Kraft process, alkaline-oxygen pulping and the Rapson effluent-free Kraft process, both reduce the total amount of organic material discharged. Neither process uses radically new chemistry or introduces any synthetic organic substances which could eventually appear in effluent streams.

The base case mechanical pulping process also discharges wood-derived organic material into water and solid waste streams. There are no significant air emissions. The process option, thermo-mechanical pulping, while resulting in slightly higher quantities of organic material discharged into water and solid waste streams, allows more effective use of low-grade wood, thereby conserving resources. No new water (or air) emission problems of any consequence can be visualized.

The base case manufacture of newsprint is a mix of Kraft pulp manufacture and mechanical pulp manufacture. The process option, the de-inking of old newsprint, while introducing small quantities of synthetic organic material and having a slightly higher treated wastewater pollutional load, results in a significant overall reduction in solid waste generation by using an existing source of solid waste as the raw material. Carbon black and dyes in the discharge may be of concern in the future.

A qualitative comparison of the organic waste discharges is presented in Table 3.

OLEFINS

Production of Ethylene by Ethane-Propane Cracking

Base Case Discharge of Organic/Toxic Pollutants--

The base case ethylene production unit discharges air, water, and solid waste streams that contain a variety of organic and inorganic pollutants.

There are five major sources of wastewater in the base case ethylene production unit:

- Decoking scrubber effluent,
- Dilution steam blowdown,
- High-pressure steam blowdown,
- Acid gas scrubber water, and
- Non-contact cooling water blowdown.

Except for non-contact cooling water blowdown, the major process wastewater streams are usually combined into a single stream and sent to a central wastewater treatment facility. The combined wastewater contains a variety of hydrocarbon pyrolysis products, dissolved inorganic carbonates, sulfates, sulfides, and other salts, and suspended solids (mostly carbonaceous particulates). It is quite common for non-contact cooling water blowdown to contain chromium compounds which are used as corrosion inhibitors. Generally, the pollutants of greatest concern are the hydrocarbons and various sulfur compounds which are characterized by non-specific parameters such as biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The wastewater is typically subjected to suspended solids removal followed by biological treatment. Even though the treated effluent still contains appreciable amounts of organic matter, it is not generally considered toxic--certainly not in the same degree as high-concentration synthetic organic residues. A detailed description of wastewater effluent loadings, treatment technology, and costs is presented in Volume VI, pages 90-100.

The major solid wastes are wastewater treatment sludge and spent dessicants. The sludge produced by the wastewater treatment processes contains large quantities of relatively inert carbon particulate matter ("coke"), biodegradable solids from the waste micro-organisms in the biological treatment system, and many of the previously listed pollutants originally present in the raw wastewater. The sludge is often dewatered by mechanical means prior to landfill. Spent dessicants are

TABLE 3. PULP AND PAPER INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
Base case Bleached Kraft pulping	Soluble and insoluble wood-derived organic material. Presence of sulfur compounds; not considered toxic. Major source of organic pollutants.	Hydrogen sulfide and organic sulfur compounds such as methyl mercaptan and dimethyl sulfide. Minor (but malodorous) source of organic pollutants.	Wet sludge from biological wastewater treatment. Sulfur compounds present, though not considered toxic. Major source of organic pollutants.
Alkaline-oxygen pulping	Soluble and insoluble wood-derived organic materials. Smaller amount of sulfur compounds than base case. Quantity of total organic pollutants somewhat less than base case.	Elimination of the discharge of malodorous sulfur compounds to the air.	Wet sludge from biological treatment. Smaller amount of sulfur compounds than base case. Quantity of total organic pollutants somewhat less than base case.
The Rapson effluent-free Kraft process	Soluble and insoluble wood-derived organic materials. Quantity of total organic pollutants significantly less than base case.	Air emissions expected to be essentially the same as the base case kraft process.	Wet sludge from biological treatment. Quantity of total organic pollutants significantly less than base case.

(continued)

TABLE 3 (Continued). PULP AND PAPER INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
Base case mechanical pulping	Soluble and insoluble wood-derived organic materials. Major source of organic pollutants.	No significant emission of organic material.	Wet sludge from biological treatment. Major source of organic pollutants.
Thermo-mechanical pulping	Soluble and insoluble wood-derived organic materials. Quantity of organic pollutants slightly greater than base case.	No significant emission of organic material.	Wet sludge from biological treatment. Quantity of organic pollutants slightly greater than base case.
Base case manufacture of newsprint	Discharges are a mixture of those of the conventional kraft process and mechanical pulping.	Discharges are a mixture of those of the conventional kraft process and mechanical pulping.	Discharges are a mixture of those of the conventional kraft process and mechanical pulping.
De-inking of old news for newsprint	Wood-derived organic materials plus synthetic and petroleum-derived organic material from ink. Major source of organic pollutants.	No significant emission of organic material.	Wet sludge from de-inking operation and from biological treatment. Use of old news greatly alleviates overall solid waste disposal problems.

solid particles typically composed of silica gel, alumina, or ceramic molecular sieve material. The dessicants themselves are relatively inert, but they can be contaminated with hydrocarbons. The spent dessicant solid waste stream is many times smaller than the wastewater treatment sludge stream. Neither is generally considered toxic.

Organic pollutants present in air emissions are mainly in the form of carbonaceous particulate matter and hydrocarbon vapors. Particulate matter is emitted from coking and related operations and is largely removed by wet air pollution control devices. Hydrocarbons are discharged to the air largely as the result of fugitive emissions from the following sources:

- Compressor, valve, and pump seals;
- Emergency venting and startup;
- Periodic maintenance operations requiring the flushing of heat exchangers, pipes, and so on; and
- Miscellaneous leaks and spills.

Although many of the hydrocarbon emissions can be piped to the plant flame and combusted, a significant amount of hydrocarbon vapors (mainly ethylene) do eventually escape to the atmosphere.

Process Option 1 - Production of Ethylene from the Pyrolysis of Naphtha--

Because of the foreseeable shortage of natural gas, and hence the declining availability of ethane and propane, more and more domestic ethylene production is being based on heavier petroleum products. One option is the pyrolysis of naphtha. Conceptually, naphtha cracking is quite similar to ethylene cracking. A detailed process description is given in Volume VI, pages 22-26. While the total energy demand for a naphtha cracker is larger on a per-unit-ethylene basis, so much more co-product material is produced that the energy consumption per unit of net hydrocarbon product is smaller than for ethylene-propylene cracking.

The production of ethylene from the pyrolysis of naphtha also generates air, water, and solid waste streams that contain organic pollutants. Qualitatively, the wastewater from naphtha cracking is not unlike that from the base case technology. No different wastewater streams are added, and no existing wastewater streams are eliminated. While the exact composition of the individual wastewater streams cannot be precisely calculated on a generalized basis, the similar process sources would be expected to result in similar compositions. The wastewater flow rate from an ethylene plant based on naphtha cracking is expected to be approximately 1.7 times that of the base case plant. It is, therefore, likely that the quantity of organic

pollutants in the wastewater would be approximately 1.7 times that of the base case plant, assuming biotreatment at the same efficiency.

As in the case of the base case technology, most of the solid waste generated by the production of ethylene from naphtha cracking is wastewater treatment sludge. Its composition is expected to be quite similar to that of sludge generated by the base case technology. The quantity of wastewater treatment sludge is expected to be 1.7 times that of the base case plant. The quantity of spent dessicants is expected to be the same as the base case plant. An additional solid waste stream composed of recovered sulfur is generated by naphtha cracking. It will probably contain small amounts of organic material.

The production of ethylene from the pyrolysis of naphtha results in an increase in air emissions over the base case technology. More particulate matter is generated due to the required increase in furnace capacity and the increased frequency of decoking. In addition to the base case emissions of hydrocarbons, the production of ethylene from naphtha cracking will result in hydrocarbon emissions from the storage of liquid hydrocarbon feedstocks. (When ethane and propane are processed, the feedstocks arrive at the plant either in pressurized storage tanks or via pipeline. On the other hand, the heavy feedstocks may be stored in petroleum storage tanks, which, even if equipped with floating roofs, undergo evaporative losses.) The increase in hydrocarbon emissions is significant. The nature of the volatile hydrocarbons is not considered to be toxic in the usual sense.

Process Option 2 - Production of Ethylene from Gas-Oil Cracking--

Also a natural gas-conserving option, ethylene production from gas-oil cracking is technically quite similar to that of naphtha cracking. A detailed process description is presented in Volume VI, pages 27-31. As in the case of ethylene production by naphtha cracking, the composition of the combined wastewater stream is expected to be quite similar to that of the base case ethylene plant. The wastewater flow rate, however, will be approximately 3 times greater than the base case. We can, therefore, expect the quantity of organic pollutants in the treated effluent to be 3 times that of the base case plant. The wastewater treatment sludge generated by ethylene production from gas-oil cracking is similar in composition to that of the base case ethylene plant, but will be generated at a rate that is 3 times greater. Gas-oil cracking also produces a recovered sulfur waste stream. It is expected to be 1.8 times the size of that produced by the naphtha cracking process option. (The base case process essentially has no sulfur waste stream.) The composition and size of the spent dessicant waste stream are expected to be about the same as those of the base case ethylene plant.

As in the case of the naphtha-cracking process option, gas-oil cracking will result in an increase in fugitive hydrocarbon emissions over the base case ethylene plant, primarily as the result of storing liquid hydrocarbon feedstock. However, the quantity of hydrocarbons

emitted is expected to be somewhat less than that of the naphtha cracking process option.

Summary

The base case ethylene production unit discharges air, water, and solid waste streams that contain organic pollutants. The waste streams are not generally considered toxic.

Both process options--naphtha cracking and gas-oil cracking--will result in an increase in the quantity of organic pollutants discharged in the treated wastewater stream. Also, both process options will result in an increase in the quantity of wastewater treatment sludge and will also introduce a new solid waste stream--namely, recovered sulfur.

Due to the necessity for storing liquid hydrocarbon feedstocks, both process options will result in an increase in the amount of hydrocarbons that escape to the atmosphere.

A qualitative comparison of the organic/toxic pollutants is presented in Table 4.

AMMONIA

Manufacture of Ammonia from Natural Gas

Base Case Discharge of Organic/Toxic Pollutants--

The manufacture of ammonia from natural gas has associated with it very few environmental problems. A schematic representation of the process, showing the potential air, water, and solid waste emissions, is given in Volume VII, Figure 2.

Wastewater streams consist of cooling tower blowdown, boiler blowdown, compressor blowdown, and process condensates. With the exception of cooling tower blowdown, the wastewater streams are relatively small. Cooling tower blowdown can sometimes be contaminated with corrosion inhibitors composed of chromium compounds. In the remaining wastewater streams, ammonia is the principal contaminant. The wastewater contains only small amounts of organic material.

The main air pollution problem associated with the production of ammonia from natural gas is the loss of ammonia to the atmosphere from various sources within the plant. There are no significant emissions of organic pollutants to the atmosphere.

There are two sources of solid waste from the manufacture of ammonia from natural gas:

- Wastewater treatment sludge, and
- Waste catalyst.

TABLE 4. OLEFINS INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
Base case production of ethylene by ethane-propane cracking	Treated effluent contains hydrocarbon pyrolysis products and carbonaceous particulate matter. Non-contact cooling water may contain chromium compounds.	Fugitive hydrocarbon emissions from vents, leaks, and spills.	Wastewater treatment sludge containing hydrocarbon pyrolysis products, carbonaceous particulate matter, and waste microorganisms. Small amount of hydrocarbon-contaminated spent dessicant.
Process Option 1: Naphtha cracking	Same composition as base case. Quantity of organic pollutants is approximately 1.7 times that of base case.	Increase in fugitive emissions over base case due to storage of liquid hydrocarbons.	Increase in wastewater treatment sludge over base case. Introduction of a recovered sulfur waste stream. Spent dessicants same as base case.
Process Option 2: Gas oil cracking	Same composition as base case. Quantity of organic pollutants is approximately 3 times that of base case.	Increase in fugitive emissions over base case due to storage of liquid hydrocarbons.	Increase in wastewater treatment sludge over base case and naphtha cracking. Larger recovered sulfur stream than naphtha cracking.

The quantity of wastewater treatment sludge is quite small. The sludge contains inorganic particulate matter such as rust, oil and grease, small amounts of ammonia, and chromium compounds (if chromate corrosion inhibitors are used in the cooling water system). Waste catalyst is composed of iron oxide. Neither can be considered a serious problem.

Process Option 1 - Manufacture of Ammonia from Coal--

Given the shortage of natural gas, and the need for the United States to reduce its dependence on foreign petroleum, serious consideration should be given to basing future ammonia plants on coal. Prior to World War II, nearly all synthetic ammonia production was based on the use of coal to produce synthetic gas for the actual ammonia production step. Since that time only a small number of ammonia plants based on coal have been built. A detailed description of the process is presented in Volume VII, pages 37-45.

The use of coal as a feedstock for the manufacture of ammonia results in pollution problems that are far more serious than those associated with the production of ammonia from natural gas.

In addition to the base case wastewater streams, an ammonia plant based on coal will have the following wastewater streams:

- Coal pile runoff;
- Slag and ash pile runoff;
- Cooling tower blowdown (over and above the base case cooling water blowdown) and
- Wastewater from the synthesis gas purification system.

Rainwater runoff from coal piles is slightly acidic and would contain particulates, organic compounds, and heavy metals leached out of the coal by the rainwater, and oxidation reaction products. Heavy metals are the pollutants of greatest concern in this wastewater stream. A representative distribution of heavy metals in coal, slag, and fly ash is presented in Volume VII, page 54. Many of these constituents could be leached.

The carbon dioxide and hydrogen sulfide removal system (Rectisol) and the sulfur recovery plant tail gas cleanup system produce wastewater streams that must be treated. The wastewater streams contain methanol and other organic compounds as well as hydrogen sulfide. Many of the organics are expected to be biodegradable.

The use of coal greatly increases the quantity of solid waste generated. In addition to the base case solid waste streams previously described, the manufacture of ammonia via coal gasification generates the following solid waste streams:

- Slag - A waste slag, largely composed of the ash content of the coal, is produced in the coal gasification step. An

elemental analysis of the slag is presented in Volume VII, Table 19, page 54. The slag contains leachable heavy metals and therefore presents a disposal problem. Very large quantities of slag are produced (0.182 ton/ton NH_3).

- Runoff Treatment Plant Sludge - Since large quantities of coal and slag must be stored on site, contaminated stormwater runoff is a major water pollution problem associated with the coal gasification alternative. The primary pollutants of concern in the runoff water are heavy metals. Therefore, the proposed wastewater treatment system consists of precipitation (with lime) and settling, which produces a secondary waste sludge composed of metal hydroxides.

- Synthesis Gas Purification Wastewater Treatment Plant Sludge - The wastewater from the synthesis gas purification step contains biodegradable organic material and hydrogen sulfide. If proper design criteria are followed, it can be treated in a high detention time biological treatment system. The biological treatment system will produce a small sludge stream largely composed of waste microorganisms and a small amount of unoxidized methanol and sulfide in the liquid fraction.

- Recovered Sulfur - The sulfur removed from the coal during the gasification step is recovered as molten sulfur. In our analysis it was assumed that this byproduct sulfur would be marketed. If market conditions are such that all of the sulfur cannot be sold, it will become a solid waste stream destined for land disposal, but it is not considered a severe problem.

The use of coal as a feedstock for ammonia production is expected to have the following impact on air emissions:

- Coal Receiving and Storage - The use of coal will require facilities for unloading and storage, coal grinding, and conveying to the process--all of which generate particulate emissions.

- Synthesis Gas Production - The use of coal introduces a significant amount of sulfur which must be removed from the gas stream.

- Ammonia Production, Storage, and Unloading - The emissions from the actual ammonia manufacturing operations are expected to be the same as the base case.

While the air pollution problems associated with the use of coal are quite significant, the major pollutant of concern is sulfur rather than organic/toxic pollutants (see Sulfur Oxides report).

Process Option 2 - Production of Ammonia from Heavy Fuel Oil--

This process option is also intended to conserve natural gas. In the early 1950's, industrial processes were developed for producing a synthesis gas, carbon monoxide, and hydrogen by the partial oxidation of hydrocarbons. In producing ammonia from heavy fuel oil, the fuel oil is first converted into synthesis gas which is then processed (in a manner almost identical to that used in the coal gasification alternative) to form a feedstock for the actual ammonia-producing step. A detailed description of the process is presented in Volume VII, pages 66-79.

The production of ammonia from heavy fuel oil results in a significant increase in the base case air, water, and solid waste pollution problems. However, these are less serious than the pollution problems associated with the production of ammonia from coal.

In addition to the base case wastewater streams, the production of ammonia from fuel oil results in a synthesis gas purification stream that has about the same flow rate and characteristics as that produced in the ammonia-from-coal option. There is also a wastewater stream from the sulfur recovery unit and a stream from the soot recycle system. The use of fuel oil instead of coal eliminates the contaminated rainwater runoff problem from coal and slag piles. Overall, the water pollution problems resulting from the use of fuel oil are less than those associated with the ammonia-from-coal option.

In addition to the base case solid waste streams, the following solid waste streams are generated in the production of ammonia from fuel oil:

- Wastewater Treatment Sludge - The wastewater streams contain biodegradable organic matter and therefore can be treated in biological treatment systems. A waste sludge is produced which contains waste micro-organisms and some of the organic pollutants originally present in the wastewater. The amount of sludge is far less than that produced by the ammonia-from-coal option and does not contain appreciable amounts of heavy metals.

- Recovered Sulfur - As in the case of the production of ammonia from coal, sulfur is removed from the oil and presumably sold as a byproduct in the form of molten sulfur. The rate of sulfur generation is significantly less than for the ammonia-from-coal process option.

The air pollution resulting from oil gasification is less than that associated with the ammonia-from-coal process option. There is no coal-related dust source. The only significant air emission is the sulfur-laden exhaust from the carbon dioxide and hydrogen sulfide removal systems.

Summary

The base case technology involving the production of ammonia from natural gas has very few environmental problems. There is a minimal discharge of organic pollutants, and the waste streams are not generally considered toxic.

The process option based on the use of coal as a feedstock greatly increases the air, water, and solid waste pollution loads over the base case technology. Heavy metals present in both coal and slag, and which eventually appear in the treated wastewater and sludge streams, create a much more serious pollution problem than the waste streams from the base case technology. There is also a significant increase in the organic pollutants appearing in water and solid waste streams.

The process option based on the gasification of fuel oil also results in a significant increase in the base case pollution load, but to a lesser degree than the ammonia-from-coal process option. Heavy metals are not a major problem, as they are in the coal option.

A qualitative comparison of the organic/toxic pollutant discharges is presented in Table 5. Organic/toxic pollutants other than those found in any use of coal do not appear to be of a magnitude that would influence decision-making.

ALUMINA/ALUMINUM

The aluminum industry is comprised of two basic operations: (1) the production of alumina (Al_2O_3) from aluminum-bearing minerals, and (2) the reduction of alumina to aluminum metal. The two operations are conducted at entirely separate locations.

Production of Alumina by the Bayer Process

Base Case Discharge of Organic/Toxic Pollutants--

At present, the sole technology used to produce alumina in the United States is the Bayer process. It is applicable only to bauxite as a raw material, most of which is imported from the Caribbean, northern South America, and Australia.

In the Bayer process (which is described in detail in Volume VIII, pages 106-118), finely ground bauxite is digested at elevated temperatures under pressure. The digesting liquor contains sodium aluminate and free caustic. After the digestion step, the insoluble components of the bauxite, primarily the oxides of iron, silica, and titanium, are removed by thickening and filtration. The aluminum-containing liquor is then subjected to a series of precipitation, separation, and calcination steps to yield the final product--alumina.

TABLE 5. AMMONIA INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
Base case production of ammonia from natural gas	Cooling tower blowdown sometimes contaminated with chromium plus small ammonia-contaminated process streams. Virtually no organic pollutants.	Losses of ammonia from storage and processing facilities. No significant discharge of organic pollutants.	Small quantities of wastewater treatment sludge and waste catalyst. Very minor source of organic/toxic pollutants.
Process Option 1: Production of ammonia from coal	Base case discharge plus heavy metal-containing coal and slag pile runoff, plus process wastewater streams containing organic pollutants. Major increase in base case organic/toxic pollutant discharge.	Base case discharge plus particulate matter from coal handling, plus sulfur emissions from synthesis gas production. No significant discharge of organic pollutants.	Base case discharge plus very large quantities of heavy metal-containing slag and runoff treatment sludge, plus wastewater treatment sludge containing organic pollutants. Very large increase in base case organic/toxic pollutant discharge.
Process Option 2: Production of ammonia from heavy fuel oil	Base case discharge plus process wastewater containing organic pollutants. Major increase in base case organic/toxic pollutant discharge, but less than that of the coal process option.	Base case discharge plus sulfur emissions from synthesis gas production. No significant discharge of organic pollutants.	Base case discharge plus wastewater treatment sludge containing organic pollutants. Very large increase in base case organic/toxic pollutant discharge, but less than coal process option.

Solid Waste - The separated solids, known as "red mud," are discarded, usually into large tailing ponds. The quantity of red mud removed from the caustic slurry following digestion varies with the bauxite used and can range from 0.33-2.0 tons (dry basis) per ton of alumina produced. About 0.8 ton per ton of alumina is typical in U.S. plants.

The composition of red mud is presented in Volume VIII, Table 1, page 121. The solid fraction, in addition to containing the oxides of iron, silicon, and titanium, also contains undissolved alumina, phosphates, lime, and manganese oxide. Various trace heavy metals may also be present and would constitute the only "toxic" waste. The liquid fraction of the red mud is highly alkaline (typically pH 12.5) and contains high concentrations of caustic, soda ash, sodium chloride, and dissolved alumina. The disposal of red mud constitutes the largest environmental impact associated with alumina production.

Wastewater - While the flow rate of the red mud stream is quite large, most of the water fraction is recycled after the red mud is deposited. Other wastewater streams consist of spent alkaline process liquors, condensates, cooling water, and stormwater runoff. Many of these streams can be used as red mud transport water if the overall water balance of the plant is favorable. In fact, a major segment of the industry operates its wastewater systems in essentially a zero-discharge mode. Small quantities of heavy metals may also be present in the wastewater streams of those plants that occasionally or continuously discharge wastes.

Air Emissions - Particulates, originating from the bauxite ore and evolved during the various grinding and calcining steps, constitute the major air emission from alumina production.

Process Option 1 - Production of Alumina from Domestic Clays via Hydrochloric Acid Leaching--

The impetus for employing this process is not energy conservation (it actually uses more energy than the base case Bayer process), but rather to reduce the dependence on foreign sources of raw material. The hydrochloric acid and other alternatives to the Bayer process are based on the extraction of alumina from the large reserves of kaolin clay in Georgia and South Carolina.

The hydrochloric acid process is described in detail in Volume VIII, pages 23-30. Briefly, in the hydrochloric acid process, clay is dehydrated, leached with hydrochloric acid, and then settled to separate the residue from the aluminum chloride/iron chloride solution. This solution is then purified with an amine ion exchange system operation to remove the iron chloride, while leaving the aluminum chloride in solution. The aluminum chloride is crystallized from the solution and decomposed to alumina, and the acid value is recovered.

Solid Waste - The primary waste material from this process is the underflow from the series of thickeners, which consists of the acid-insoluble clay fraction and a dilute aluminum chloride aqueous solution. The composition of this solid waste stream is given below (Volume VIII, page 28):

Constituent	Weight percent
Alumina (undissolved)	12.8
Silica	33.5
Aluminum chloride (soluble)	0.6
Other soluble chlorides (mostly iron)	1.5
Other impurities (Mg, Ti, P, V, SO_4)	2.7
Water	48.9
Total	100.0

This waste material will also very likely be contaminated with small quantities of kerosene, alcohol, and amines, all of which originate from the ion exchange loop.

On a dry basis, this waste is generated at a rate of approximately 3.35 tons per ton of alumina, which is about 4 times greater than the typical 0.8 ton per ton rate for conventional bauxite refining plants. The main reason for this tremendous increase in solid waste is the low alumina content of kaolin clay as compared to bauxite. The characteristics of the waste are also quite different. Instead of the liquid fraction of the waste being highly alkaline, it is acidic and contains high concentrations of chlorides. This chemical environment is far more conducive to the dissolution of many trace heavy metals than the alkaline conditions present in red mud from bauxite refining.

Wastewater - As in the case of the base case alumina process, most if not all of the water will be recycled through the solid waste impoundments. If a water discharge is unavoidable, it will very likely contain chlorides, small quantities of the above listed organic materials, and the heavy metals contained in the clay as soluble chlorides.

Air Emissions - Since grinding and calcination operations are involved, this process will generate particulate matter in much the same way as bauxite refining. In addition, the acid recovery plant generates a tail gas stream that may contain HCl. It will most likely have to be controlled by wet scrubbing, with the spent scrubber water discharged to the tailings pond.

Process Option 2 - Production of Alumina from Domestic Clays via Nitric Acid--

Also intended for the extraction of alumina from domestic kaolin clay, the nitric acid process (described in detail in Volume VIII, pages 30-38) involves the following basic steps:

- Calcining the kaolin clay to make the contained alumina selectively available for extraction with nitric acid.
- Leaching the calcined clay with hot nitric acid at atmospheric pressure to produce a solution of aluminum nitrate and a suspension of clay insolubles.
- Separating the clay insolubles from the aluminum nitrate liquor in thickeners.
- Removing the iron and other impurities from the clarified aluminum nitrate liquor by use of a liquid ion-exchange medium.
- Removing the remaining impurities from the iron-free aluminum nitrate liquor by means of vacuum crystallization of aluminum nitrate nonohydrate.
- Recovering the alumina by hydrolysis of the aluminum nitrate under controlled conditions so that the nitrate values are recovered largely as nitric acid rather than as nitric oxides.
- Recovering the nitric acid and nitrogen oxide values in the form of nitric acid for recycle.
- Calcining the product alumina.

Solid Waste - The primary waste material from this process is the underflow wet sludge from the series of thickeners, which consists of the acid-insoluble clay fraction and a dilute aluminum nitrate aqueous solution. The composition of this waste stream is given below (Volume VIII, page 37):

Constituent	Weight percent
Alumina (undissolved)	1.5
Silica	45.0
Aluminum nitrate (soluble)	1.9
Other soluble nitrates	2.2
Water	47.2
Other impurities (Mg, Ti, P, V, SO_4)	2.2
Total	100.0

On a dry basis, this waste is generated at a rate approximately 1.9 tons per ton of alumina, which, although lower than that for the hydrochloric acid process, is still about double that of conventional bauxite refining.

The waste is acidic, and the pollutants of major concern are the soluble nitrates, which, in general, pose more of a threat to groundwater than either the chlorides from the hydrochloric acid process or the alkaline solutions from the conventional bauxite refining process. In addition, the waste will be contaminated with small amounts of kerosene and organic phosphate ion-exchange liquid, as well as trace heavy metals from the clay itself.

Wastewater - As in the base case bauxite refining process and the hydrochloric acid process, it will be possible to recycle the bulk, if not all, of the wastewater generated. If a wastewater discharge is unavoidable, it will be contaminated with small quantities of the previously mentioned organic matter, heavy metals, and nitrates.

Air Emissions - The calcination of beneficiated clay pellets would not generate as much particulate matter as the calcination of bauxite, but dust emission controls will still be required for clay particulate as well as for fly ash removal, since coal could be used in the calcination kiln. This process also generates several waste gas streams containing oxides of nitrogen. Control of these streams is part of the total process.

Process Option 3 - Clay Chlorination (Toth Alumina) Process--

The Toth Aluminum Corporation (TAC) has been developing a process for the production of alumina and byproducts from clays and other alumina-containing minerals. The process involves the chlorination of alumina-containing raw materials in the presence of carbon to produce aluminum chloride vapor and other volatile chlorides. These are subsequently purified to remove other metal chlorides and then oxidized to produce alumina and chlorine for recycle. Based on kaolin clays, the steps in the process involve: (1) ore drying and calcination; (2) chlorination in which the aluminum, titanium, and iron present in the ore are carried overhead as volatile chlorides; (3) separation of the other chlorides from the aluminum chloride by fractional condensation and distillation; and (4) separate oxidation of the iron, silicon, and titanium chlorides to their respective oxides for recovery of chlorine for recycle. Finally, the aluminum chloride, after separation, is also oxidized to produce alumina and to regenerate chlorine for recycle. A detailed description of the process is given in Volume VIII, pages 37-49.

Solid Waste - The process produces a waste stream which contains the gangue materials present in the clay. An estimated composition of the waste stream is given as follows:

Constituent	Weight percent
Aluminum (insoluble)	6.0
Silica	73.7
Iron (ferric) oxide	0.8
Soluble chlorides	2.2
Other impurities	6.8
Water	10.5
Total	100.0

The rate at which this waste is generated is estimated to be approximately 1.5 tons (dry basis) per ton of alumina.

Although the solid waste streams are produced in an essentially dry state, water is used in the process, and liquid waste control will very likely involve the recycling of wastewater through the disposal lagoon, so the same type of wet tailings pond situation will be created as in HCl leaching. As in the case of the hydrochloric acid process, the pollutants of greatest concern are soluble metal chlorides.

Wastewater - The only anticipated wastewater actually discharged is cooling tower blowdown, which is often contaminated with chromium corrosion inhibitors.

Air Emissions - Three potential emission streams (described below) are apparent from this technology:

(1) The exhaust from the chlorinator, after cooling and scrubbing to remove the chlorides, will contain CO, CO_2, and probably traces of HCl, if moisture, chlorine, and the more volatile titanium and silicon tetrachlorides are present. We expect that some chlorinated hydrocarbons would result from the chlorination of heavy volatile material remaining in the coke. We would also expect that these materials would be removed in the low-temperature condensation step required to remove the titanium and silicon tetrachlorides. When these materials are oxidized at high temperature to recover the chlorine values for recycle, the chlorinated hydrocarbons are also destroyed.

(2) The dry residue from the chlorinator contains the ash from the clay and coke, alumina, and non-volatile chlorides of the alkali and alkali earth metals present in the clay and coke ash.

(3) In separating alumina from $AlCl_3$ vapor and chlorine following oxidation, residual chlorine and $AlCl_3$ may

be present in the solid alumina. The same may also occur in the oxidation of silicon and titanium tetrachlorides. We have assumed that the sources of chlorine emission would be controlled because there is a real economic incentive to conserve it and to prevent escape of this hazardous gas, although it is not one of the criteria pollutants.

The emission rates for this process depend upon purge and exhaust rates which, for the most part, are unknown at present.

Aluminum Production by the Hall-Heroult Electrolytic Reduction Process

Base Case Discharge of Organic/Toxic Pollutants--

The Hall-Heroult electrolytic reduction process is presently used to produce all of the primary aluminum throughout the world. A detailed process description is presented in Volume VIII, pages 112-118. Basically, the alumina is dissolved in molten cryolite (Na_3AlF_6) in an electrolytic cell wherein aluminum is liberated at the cathode and oxygen at the anode. The oxygen liberated at the anode reacts with the carbon anode to produce CO_2 and CO. Modern Hall-Heroult electrolytic cells are largely steel boxes lined with insulating refractory and carbon. Carbon blocks at the bottom of the cell serve as the cathode in the electric circuit. The anodes are also carbon suspended in the electrolyte from above.

Wastewater - The main sources of wastewater from primary aluminum production are the wet scrubbers used to control air emissions from the various in-plant operations and the cooling water blowdown. The following chemical constituents were found to be present in wastewater from primary aluminum production:

Suspended solids,
Dissolved solids,
Chemical oxygen demand (COD),
Oil and grease,
Fluoride,
Chloride,
Sulfate,
Free cyanide, and
Trace metals (including zinc, copper, and nickel).

Fluoride is generally considered the pollutant of greatest concern with respect to wastewater treatment. Lime neutralization/precipitation, which is standard treatment, is only partially successful in its removal.

Solid Waste - Minor amounts of solid wastes originate from the handling, storage, and feeding of raw and consumable materials (alumina, calcined coke, cryolite, and aluminum fluoride) brought into the smelter. Emissions of these materials are largely in the form of dust from handling and feeding to the cells and the anode-making operations.

However, the rebuilding of cells is a major source of solid waste from an aluminum smelter. When a cell reaches the end of its useful life and has to be rebuilt, it is removed, dismantled, and rebuilt. This operation generates a good deal of solid rubble and waste solid materials. Most of the refractory internals are impregnated with cryolite and aluminum fluoride. These materials are typically leached to recover the fluorides for reuse. The quantity of this waste varies greatly from plant to plant, depending on the procedures used.

Another major solid waste stream from aluminum production is the result of air pollution control intended for the collection of particulate matter and fluorides. If wet air pollution devices are used, the scrubber water must be treated for the removal of suspended solids and fluorides. Lime treatment is typically used to precipitate the fluorides as calcium fluoride.

Air Emissions - The electrolytic reduction of aluminum produces a CO exhaust at the anode of the cell. As the exhaust leaves the cell, it entrains particulates including fluoride salts. The exhaust also contains noxious gases, such as hydrogen fluoride and hydrogen sulfide. The manufacture of carbon anodes and their subsequent degradation produce emissions of hydrocarbons, sulfur, compounds, and particulates. These are removed as part of the air emission control system and then become wastewater constituents.

Process Option 1 - Production of Aluminum by the New Alcoa Process--

Precise details concerning this process are not available. Basically, the feed alumina is converted to aluminum chloride by chlorination in the presence of carbon to form volatile aluminum chloride. This, in turn, is purified and fed to an electrolytic cell to produce molten aluminum at the cathode and chlorine at the anode. The chlorine is recycled to the chlorination step. A description of the process is given in Volume VIII, pages 57-64.

Wastewater - Since alumina is the basic raw material for both the Hall-Heroult process and the ALCOA chloride process, those waterborne pollutants (such as heavy metals) emanating directly from the alumina itself will be substantially the same. However, the ALCOA process eliminates the use of the fluoride-containing fluxing agent. Therefore, fluoride will not be present in the scrubber

wastewater stream. On the negative side, the ALCOA process will introduce large amounts of sodium chloride into the wastewater discharge.

The ALCOA process uses very large amounts of cooling water. If chromium corrosion inhibitors are used in the cooling water circuits, they will also appear in the cooling tower blowdown.

Solid Waste - A number of solid waste streams are discharged by the ALCOA process. A waste sludge periodically removed from the electrolyte would be predominantly composed of sodium aluminate contaminated with NaCl/LiCl, and would be quite soluble. There is also a purge stream composed of unchlorinated alumina. Since the process involves coke-making to supply the carbon, it is quite possible that sulfur dioxide will have to be controlled. If so, a calcium sulfate/sulfite sludge would be produced.

Air Emissions - During the chlorination part of the process, alumina, carbon (from cracked No. 6 fuel oil), and chlorine are contacted in a fluidized state. It is possible that chlorine could react with certain residual hydrocarbon compounds to form chlorinated hydrocarbons, many of which are considered toxic pollutants. If indeed this phenomenon does occur and is found to be a serious problem, one possible solution is the installation of a combustion chamber to incinerate the chlorinated hydrocarbons.

The coke-making process produces an exhaust gas which contains sulfur dioxide and will very likely have to be subjected to sulfur dioxide removal. The exhaust gas from the HCl absorber contains carbon monoxide, carbon dioxide, minor amounts of HCl, and perhaps traces of chlorine.

The ALCOA cells use inert carbon cathodes which means that no significant amount of carbon oxide gases is released at the anode. With inert ALCOA cathodes, we expect that emissions in the baking process are significantly reduced when compared to conventional technology using consumable cathodes (Hall-Heroult prebaked cathodes or Soderberg cathodes).

Process Option 2 - Refractory Hard Metal Cathodes--

Refractory hard metal cathodes, made from zirconium and titanium carbides and borides and mixtures thereof, have been considered as potential replacements for the conventional carbon cathodes. They exhibit operational and energy conservation advantages. A description of this process innovation is presented in Volume VIII, pages 68-77.

We expect that the use of such cathodes will not appreciably change the nature or size of the base case water, air, and solid waste discharges.

Summary

The base case technology for producing alumina is the Bayer process which uses bauxite as the alumina-containing raw material. The Bayer process does not discharge any organic pollutants in water, air, or solid waste streams. The disposal of very large quantities of red mud, the insoluble residue that remains after alumina extraction, constitutes the chief environmental problem associated with alumina production. The red mud is highly alkaline and contains small quantities of heavy metals.

Alumina production from domestic kaolin clays by the hydrochloric acid and nitric acid leaching processes results in even larger quantities of waste residues, which also contain heavy metals. The wastes from these two processes are acidic rather than alkaline and contain small amounts of organic reagents used in the processing. The disposal of these wastes will pose even more of a problem than the red mud produced by the Bayer process. Heavy metals would be the major problem, both in sludges and in wastewater discharges. Nitrate is another problem of some potential concern.

The Toth alumina process, also intended for the extraction of alumina from domestic clay, produces a dry residue not unlike the solid fraction of the waste produced by the hydrochloric acid leaching process. The waste would probably be slurried and disposed of in a tailings pond in much the same manner as the other processes. Unless proper air pollution controls are used, it is possible for volatilized titanium and silicon tetrachlorides to be emitted into the air.

Aluminum production by the base case Hall-Heroult process discharges fluoride salt dust as well as hydrogen fluoride and hydrogen sulfide to the atmosphere. Wet air pollution control systems transfer some of these pollutants to the wastewater streams. When wastewater is treated for the removal of fluoride and suspended solids, a waste sludge is generated.

The new ALCOA process eliminates the use of fluoride-containing fluxing agents, but introduces large quantities of sodium chloride. The ALCOA process also produces a highly soluble waste sludge. In this process, a possibility exists for chlorinated hydrocarbons to be formed. If proper gas-handling techniques are not employed, they could be discharged to the atmosphere.

The use of refractory metal cathodes is expected to have little effect on the base case discharge of organic/toxic pollutants.

A qualitative comparison of the organic/toxic pollutants associated with the various process options is shown in Table 6.

TABLE 6. ALUMINA/ALUMINUM INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
Base case production of alumina by the Bayer process	Many plants operate in a zero-discharge mode. When water is discharged, its composition is similar to the liquid fraction of the red mud.	Particulates originating from the bauxite ore.	Large quantitites of "red mud," the insoluble residue from the bauxite ore. Highly alkaline and contains small quantities of heavy metals.
Hydrochloric acid leaching of domestic clays	May possibly be operated in a zero-discharge mode. If not, wastewater will have composition similar to liquid fraction of solid waste residue, i.e., acidic and containing chlorides, heavy metals and organics.	Particulates originating from the clay, plus small stream containing HCl.	Acid-insoluble residue generated at a rate over 4 times that of the base case. Waste is acidic and contains chlorides, heavy metals, and small quantities of organic reagents.
Nitric acid leaching of domestic clays	May possibly be operated in a zero-discharge mode. If not, wastewater will have composition similar to liquid fraction of solid waste residue, i.e., acidic and containing nitrates, heavy metals, and organics.	Particulates originating from the clay, plus some oxides of nitrogen.	Acid-insoluble residue generated at a rate of almost twice that of the base case. Waste is acidic and contains nitrates, heavy metals, and small quantities of organic reagents.

(continued)

TABLE 6 (Continued). ALUMINA/ALUMINUM INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
Process Option 3: The Toth alumina process	Cooling tower blowdown. May contain chromium corrosion inhibitors.	Unless proper air pollution controls are used, possibility of discharging titanium and silicon tetrachlorides, which will probably hydrolyze to oxides and HCl.	Solid waste composed of the rejected materials present in the clay, generated at a rate 1.5 times that of the base case. Contains soluble metal chlorides.
Base case aluminum production by the Hall-Heroult process	Wastewater streams from wet scrubbers contain some organics, cyanide, and fluoride.	Particulates containing fluoride salts, plus gaseous hydrogen fluoride and hydrogen sulfide, plus hydrocarbons.	Fluoride-contaminated cell rebuilding material plus fluoride-containing dust and wastewater treatment sludge.
Process Option 1: The new ALCOA process	Little or no fluoride present due to elimination of fluoride-containing fluxing agents, introduction of large quantities of sodium chloride. Cooling tower blowdown may contain chromium.	SO_2, small amounts of HCl, and possibly chlorine gas. The possible formation of chlorinated hydrocarbons may require the use of exhaust gas combustion chambers.	SO_2 control sludge, plus soluble sludge composed of NaCl/LiCl, purge stream of unchlorinated alumina, chromium hydroxide sludge if cooling tower blowdown is treated.
Process Option 2: Refractory hard metal cathodes	No appreciable change from base case.	No appreciable change from base case.	No appreciable change from base case.

TEXTILE

Integrated Knit Fabric Mills

Base Case Organic/Toxic Pollutants Discharge--

The base case mill produces polyester doubleknit using purchased texturized yarn. It includes the following sequence of operations (which is described in detail in Volume IX, pages 33-35): (1) yarn is first knitted into fabric in the greige mill; (2) the greige (undyed, unbleached) fabric then goes through a scouring operation to remove knitting oil, followed by dyeing, washing, and spin-drying to remove as much water as possible before hot-air drying; (3) a finish (softener/lubricant) is then applied to the fabric, which is dried and heat set. Process water is required for the scouring, dyeing, and washing operation, and this is combined into one wastewater effluent.

Most of the organic or toxic pollutants discharged from the base case integrated knit fabric mill are in the treated wastewater effluent.

A major source of organic material is the removal of knitting oil with detergent/water solutions. Knitting oils are generally based on mineral oils and certain vegetable oils. Although knitting oils do not biodegrade rapidly, they are not considered toxic.

The other major sources of organic material in the wastewater stream are the disperse dyes and dye carriers. Many dyestuffs are closely analogous in molecular structure to known carcinogenic substances, often being polycyclic, unsaturated, and highly substituted hydrocarbons. Disperse dye carriers, such as butyl benzoate, biphenyl, and others, are organic pollutants of more than moderate concern. Chromium compounds are also present in certain dyes. Disperse dyes are minute solid particles rather than in solution, and are therefore more readily removed by conventional wastewater treatment processes than water-soluble dyes.

There is a lack of quantitative data on the presence of organic materials in the treated effluents from textile mills. Organic material is usually measured indirectly in terms of gross parameters, such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), and color. To provide at least an indirect measure of the amount of organic material present in treated effluents, the proposed 1983 BATEA (Best Available Technology Economically Achievable) effluent limitations guidelines are presented as follows:

	Average daily value for 30 consecutive days shall not exceed (lb/1000 lb of product)
Biochemical oxygen demand (BOD)	1.7
Chemical oxygen demand (COD)	10-16.7
Total chromium	0.05
Phenol	0.05
Sulfide	0.10
Color	300 (color units)

Air pollution from textile mills is relatively minor and consists of low levels of particulates, such as lint, and a small amount of organic material from the finishing chemicals used.

Due to the nature of textile mill wastewater treatment systems, very little organic wastewater treatment sludge is generated. Aside from accumulated lint, the only other significant solid waste stream is the tarry residues that accumulate in the equipment used in certain hot finishing operations. The residues consist of finishing chemical degradation products, and are periodically removed and sent to landfill.

Process Change 1 - Advanced Processing--

"Advanced processing," as applied to integrated knit fabric mills, is a term referring to a collection of process changes, plant modifications, and general operational improvements which are designed to conserve both energy and water. Advanced processing consists of the following measures: use of water-soluble size, water conservation, processing at low liquor/fabric ratio, vacuum impregnation and extraction, and improved finishing techniques. These are described in detail in Volume IX, pages 28-31.

While advanced processing reduces the volume of wastewater that must be treated, it does not necessarily reduce the net pollutional loads (in terms of lb per 1000 lb of product) because approximately the same amounts of the same or very similar chemicals are used. While the lower water volumes may enable textile mills to achieve the 1983 effluent limitations more easily and at lower costs, the total quantity of pollutants discharged in the treated effluent is expected to remain very nearly the same as the base case.

Organic/toxic pollutants present in the air and solid waste streams are expected to be the same as the base case.

Process Change 2 - Solvent Systems--

A solvent-based integrated knit fabric mill is described in detail in Volume IX, pages 37-39, and would employ an organic solvent (typically perchlorethylene) instead of water for the various scouring, dyeing, and finishing operations. The contaminated solvent streams are collected and

recovered in a central solvent still. The use of solvent systems virtually eliminates wastewater effluents. A small amount of condensate from the finishing operation and from the still represents the only wastewater effluent that may contain traces of solvent and other chemicals.

Although solvent systems are currently being used for scouring synthetic knit fabrics prior to dyeing and finishing, practicable methods for complete processing, even for synthetic fibers, have not yet been developed. Thus, the various waste streams emanating from a totally solvent-based mill are not well quantified.

The escape of hydrocarbon vapors from the process poses a serious air pollution problem, and for this reason the solvent processing units are surrounded by an enclosure maintained at a negative pressure by exhausting air continuously. Exhausted air containing solvent vapors passes through an activated carbon vapor recovery system before discharge to the atmosphere. Periodically, the activated carbon is stripped with steam and the solvent vapors are returned to the solvent recovery still. According to manufacturers' data, solvent losses are about 3% of the fabric weight in present solvent-scouring systems, both as fugitive emissions and as losses within the fabric. We believe that solvent losses will have to be reduced to less than 1% to meet air quality regulations (Volume IX, page 39). Long-term losses from stored fabric may present an unexpected air pollution source.

Thus, there is a distinct possibility that implementation of solvent systems will result in a significant increase in the discharge of organic/toxic pollutants to the atmosphere. By largely eliminating the discharge of dye and dye carriers in the wastewater effluent, the amount of organic/toxic materials discharged to the aquatic environment will be greatly reduced. If the small wastewater stream from solvent finishing is incinerated, it will be eliminated altogether.

Knitting oils removed in scouring and chemicals from dyeing and finishing remain as residues in the solvent still and are removed as a solid waste for disposal. Although we have no data on either the quantity or composition of this stream, it is quite reasonable to assume that it will contain a certain amount of organic solvent. Since chlorinated organic solvents are far more environmentally objectionable than relatively inert waste textile fibers (constituting most of the base case solid waste), the possibility exists that the implementation of solvent systems will have a negative effect on the base case solid waste disposal problem.

Integrated Woven Fabric Mill

Base Case Organic/Toxic Pollutants Discharge--

Woven fabrics require a much larger sequence of processing operations than knit fabrics. Although more complex, the major processes include various combinations of scouring, washing, bleaching, dyeing, and finishing.

As in the case of the integrated knit fabric mill, most of the organic/toxic pollutants discharged from the base case integrated woven fabric mill are in the treated wastewater effluent. The combined wastewater stream from the entire manufacturing operation contains natural and processing impurities removed by hot alkaline detergents, dye material, oil and grease, and inorganic and dissolved solids. A major source of organic material is the sizing (typically polyvinyl alcohol) applied prior to weaving operations. Although polyvinyl alcohol is marginally biodegradable, it is not considered toxic. The wastewater is basically treated in the same way as wastewater from knit fabric mills, although the wastewater flow rates and concentrations are somewhat different. The proposed 1983 BATEA effluent limitations guidelines for integrated woven fabric mills are presented below (from Volume IX, page 65):

	Average daily value for 30 consecutive days shall not exceed (lb/1000 lb of product)
Biochemical oxygen demand (BOD)	2.2
Chemical oxygen demand (COD)	10-20.2
Total chromium	0.05
Phenol	0.05
Sulfide	0.10
Color	300

Air pollution and solid waste disposal problems for the base case woven fabric mill are basically the same as those associated with the base case knit fabric mill.

Process Change - Advanced Processing--

Advanced processing for woven fabrics is similar to advanced processing for knit fabrics in that it consists of a collection of process changes, plant modifications, and general operational improvements. The most important process change is the inclusion of a polyvinyl alcohol (PVA) recovery loop which takes the effluent stream from the desizing step and (after ultrafiltration) recycles the concentrated PVA solution back to sizing, and the hot water back to the desizing operation. A process flow diagram of the advanced processing steps for an integrated woven fabric mill is presented in Volume IX, page 50. This operation both conserves energy (in the form of heated water) and reduces the volume of the effluent wastewater stream. Although the raw waste loading is also somewhat reduced due to the recovery of PVA, one can expect that the net quantity of pollutants in the treated effluent would be more or less the same as that of the base case, i.e., the amount of pollutants that will satisfy the effluent guidelines limitations.

The implementation of advanced processing is not expected to have a significant effect on either the base case air pollution or solid waste disposal problem.

Summary

Of the processes examined here, solvent processing of knit fabrics can be expected to have the most significant impact on the generation and discharge of organic/toxic pollutants. Significant waterborne wastes may be replaced by solvent emissions of chlorinated hydrocarbons. The relative importance of both streams is difficult to quantify, but will undoubtedly have some impact on the industry's decisions concerning implementation of the newer technology.

A qualitative comparison of the organic/toxic pollutant discharges is presented in Table 7.

CEMENT

Manufacture of Portland Cement by the Dry Process, Long Rotary Kiln

Base Case Discharge of Organic/Toxic Pollutants--

Hydraulic cement is a powder made by burning lime, silica, alumina, iron, and magnesia together in a kiln and then pulverizing the product. The processing of raw materials into finished cement follows four steps:

- Crushing,
- Grinding,
- Clinkering, and
- Finishing grinding,

which are described in detail in Volume X, pages 84-89. The crushing, grinding, and finishing grinding are merely size reduction and material preparation steps. The heart of the process, and the operation which consumes about 70-80% of the total energy used in cement manufacturing, is the clinkering step. In the clinkering step, the accurately controlled mixture of raw materials reacts chemically at high temperatures (over 2000°F) in the kiln to produce "clinker," which is subsequently ground into cement.

Since the changes in Portland cement technology and cement industry practices examined in this study have an effect only on the clinkering operation, the analysis of organic/toxic pollutant implications have also been restricted to the clinkering operation.

No organic pollutants are present in any of the water, air, and solid waste streams associated with the clinkering step of the base case gas-fired cement manufacturing process. The chief pollutant discharged in any of the waste streams is cement dust. While small amounts of lead and chromium have been reported in wastewater streams from some cement

TABLE 7. TEXTILE INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
Base case integrated knit fabric mills	Knitting oils, dyes and dye carriers. Major source of organic/toxic pollutants.	Lint, organic materials from finishing chemicals. Minor source of organic/toxic pollutants.	Wastewater treatment sludge, lint, residues from finishing operations. Minor source of organic toxic pollutants.
Advanced processing	Essentially the same as base case.	Essentially the same as base case.	Essentially the same as base case.
Solvent systems	Drastic reduction or possible elimination of wastewater discharge.	Introduction of organic solvents will very likely increase air pollution problems. Major source of organic/toxic pollutants.	Possible solvent contamination of solid waste streams. Some increase over base case. Minor source of organic/toxic pollutants.
Base case integrated woven fabric mills	Sizing material, dyes, and dye carriers. Major source of organic/toxic pollutants.	Same as knit fabric mills.	Same as knit fabric mills.
Advanced processing	Same as base case.	Same as base case.	Same as base case.

plants, the cement dust usually is virtually free of trace heavy metals (Volume X, page 106). As a result, the effluent limitations guidelines for the cement industry place restrictions only on pH and total suspended solids. Air emission and solid waste (dust) are certainly generated, but they would not normally be considered "toxic."

Process Option 1 - Equipping the Rotary Kiln with a Suspension Preheater--

A suspension preheater is a modification to or an addition to a cement rotary kiln. It is attached to the raw feed inlet end of the kiln, totally replacing the preheating zone of the rotary kiln. A detailed process description is given in Volume X, pages 16-34. Essentially, suspension preheating conserves energy by improving heat and mass transfer and making better use of the waste heat in the combustion gases.

As in the case of the base case cement plant, the suspension preheater option will produce a waste dust, which probably will also be stored in large piles or holding ponds. The cement dust is expected to have a composition quite similar to that of the base case plant, although the fraction of soluble inorganic salts is expected to be somewhat higher. Since the same basic raw materials are used and since no organic or toxic pollutants are introduced into the process, it is reasonable to expect the waste streams to be virtually free of organic pollutants and trace heavy metals.

Process Option 2 - Installation of a Flash Calciner--

The flash calciner is a process operation intended for installation between a rotary kiln and a suspension preheater. Its use has a number of operational and energy conservation benefits, which are described in detail in Volume X, pages 34-40.

The quantity and composition of pollutants discharged from a cement operation equipped with a flash calciner are expected to be essentially the same as those of the suspension preheater option, i.e., no organic pollutants and virtually no heavy metals.

Process Option 3 - Fluidized Bed Process--

The difference between the fluidized bed cement-making process and the conventional processes is in the high-temperature clinkering step. All of the other steps are essentially identical. The fluidized bed process has many mechanical, operational, economic, and energy-related advantages over the rotary kiln manufacturing process. Of particular note is that practically any form of carbonaceous fuel can be used in the fluidized bed reactor. Also, current studies indicate that the cement process employing the fluidized bed cement reactor, with proper heat recovery, requires significantly less total energy than the conventional dry, long rotary kiln. A detailed description of the fluidized bed process is presented in Volume X, pages 40-54.

A plant using the fluidized bed process is expected to generate one-fifth of the cement dust produced by the base case plant. As in the case of the base case, no organic pollutants will be discharged, and the dust will be virtually free of trace heavy metals. An important difference, though, is that the cement dust from the fluidized bed process will consist of high-grade potassium and sodium sulfate, both of which are highly soluble and would require more careful disposal.

Process Option 4 - Conversion to Coal Fuel from Oil and Natural Gas--

The energy conservation potential of the use of coal fuel is primarily one of form rather than quantity of energy. A variety of material handling steps and process modifications are required to convert a conventional oil or natural gas-fired rotary kiln to coal. These measures are discussed in detail in Volume X, pages 60-66.

The pollutional implications associated with the use of coal in the manufacture of cement have to do with the ultimate fate of the ash content of the coal. Most of the organic air pollutants can be expected to have been oxidized by the high temperature of the clinkering. Typical bituminous coal contains approximately 10% ash by weight. Between 50% and 100% of all of the coal ash produced by the combustion of coal in a rotary cement kiln contacts and chemically combines with the clinkering raw materials, thereby losing its identity as coal ash and becoming Portland cement clinker. When using coal, however, the composition of the raw materials must be adjusted to incorporate the coal ash.

A portion of the coal ash escapes the rotary kiln with the cement dust and is eventually disposed of with the cement dust. It alters the composition of the combined waste, principally due to the presence of heavy metals in coal ash. (A composition of West Virginia coal ash is presented in Volume X, Table 22, page 73.)

The relative fractions of the coal ash which leave the plant as cement versus solid waste are highly dependent on the raw material composition, process configuration, and other site-specific factors. It is therefore not possible to quantify the overall toxic pollutant implications of using coal as a fuel in cement manufacturing. However, since the base case plant discharges virtually no toxic heavy metals, it follows that the use of coal must necessarily result in an increase in the discharge of toxic heavy metals. Since the cement dust is alkaline, it is reasonable to expect that the metals from the coal ash will not be prone to a high degree of leaching when the cement dust is exposed to water. It is very likely that more serious pollutional problems will result from the storage and handling of coal rather than from the actual process wastes. Leaching of heavy metals from concrete made with a coal-fired kiln cement has not been studied.

Summary

There is no discharge of organic pollutants and virtually no discharge of toxic pollutants (a small amount of heavy metals is sometimes present in cement dust) from the base case cement process.

The only process option that would introduce toxic pollutants into the waste streams is the one involving the conversion to coal fuel. Heavy metals are present in coal ash and can appear in waste cement dust. The storage and handling of coal also presents pollutional problems. Nevertheless, the incorporation of a portion of the coal ash into the clinker and the cement dust reduces the pollution. Consequently, use of coal, if possible, in cement clinkering would allow transfer of higher forms of energy (gas and oil) to other industries and utilities where such advantage would not be gained.

GLASS

Glass Melting

Base Case Discharge of Organic/Toxic Pollutants--

Since glass melting is by far the most energy-intensive portion of the entire glass manufacturing process, downstream finishing operations have not been included in the analysis.

The conventional glass-melting furnace is presently fired by natural gas. The major raw materials which make up a soda-lime glass (the most common type of glass) are silica sand, feldspar, dolomite, limestone, and soda ash. Small amounts of fluorspar are often added as a fluxing agent. A description of the base case glass-melting process is given in Volume XI, pages 17-32.

The escape of raw materials into air, water, and solid waste streams constitutes the major source of pollutants from the glass-melting operation. Air emissions are controlled by a two-stage process consisting of a wet scrubber followed by a bag filter. Soda ash is added to the scrubber water to remove sulfur oxides as calcium sulfate/sulfite. The scrubber water is recycled and a small purge stream discharged. It is likely that the purge stream will have to be treated with lime to precipitate fluorides and heavy metals, thereby producing a wet sludge. The bag filter collects fine particulate matter not captured by the scrubber.

Aside from carbonaceous particulates resulting from incomplete combustion of gas, there is no discharge of organic pollutants from the base case glass-melting operation. Particulate matter emitted from the furnace, and eventually introduced into wastewater and solid waste streams, contains heavy metals such as arsenic, antimony, selenium, and lead. The composition of glass-melting furnace emissions is given in Volume XI, page 27. Most of the heavy metal-containing particulates are eventually discharged from the plant as a solid waste.

Process Option 1 - Melting Energy Supplied by a Coal Gasification System--

In this process option, an on-site coal gasification system is designed to supply the entire fuel gas requirements for the melting operation, thus eliminating the dependence on natural gas. Generally, coal gasification processes include, in some variation, the following steps:

- Coal handling and storage,
- Coal preparation,
- Gasification,
- Oxidant feed facilities, and
- Gas cleaning.

The details of the process are described in Volume XI, pages 32-45.

When coal gasification is used to generate a gaseous fuel for the glass-melting furnace, the major environmental difference is not in the glass-melting process, but rather in the fuel-generating process for the furnace. The coal gasification unit generates considerable air, water, and solid waste emissions.

The fuel gas produced in the coal gasifier will contain sulfur, mainly in the form of H_2S. To prevent excessive SO_2 emissions, the sulfur is removed prior to the burning of the fuel in the glass furnace. Elemental sulfur recovery via the Stretford process is a highly applicable means of sulfur removal for the type and size of coal gasifier that would be used in a glass plant. Since the quantity of elemental sulfur recovered is too small to warrant an attempt at marketing it as a byproduct, it will very likely have to be disposed of as a solid waste. The Stretford process also produces a small wastewater stream containing many of the reagents used in the sulfur recovery process. The stream contains sodium anthraquinone disulfonate, sodium meta-vanadate, sodium citrate, sodium thiosulfate, and sodium thiocyanate. Due to the small and intermittent nature of this waste stream, it would probably be removed from the plant via contract disposal.

The disposal of very large quantities of coal ash constitutes the major addition of toxic pollutants to the base case process for it results in a four-fold increase in the quantity of solid waste generated. Coal ash contains a variety of heavy metals, the concentrations of which are highly dependent on the type of coal used. A representative composition of coal is presented in the Cement Industry Report, Volume X, page 73.

Process Option 2 - Melting Energy Supplied by Direct Coal Firing--

Direct coal firing has the advantage over other coal-firing process options in that it uses all of the heating value of the coal. To use coal directly in burners, a coal storage area is needed as well as a live coal storage bin, a pulverizer, screens, a feeder, and the pulverized coal burner(s). A coal storage area capable of storing about one month's supply appears reasonable.

Since coal is a high-sulfur fuel, a direct coal-fired glass-melting facility will require a sulfur dioxide scrubbing system. Alkaline-based SO_2 scrubbers generate solid waste in the form of calcium sulfate/sulfite sludges which also contain some of the ash content of the coal. Thus, the SO_2 scrubber sludge will contain some of the heavy metals present in the ash. As in the coal gasification alternative, large quantities of heavy metal-containing coal ash will have to be disposed of, in addition to the solid waste streams emanating from the base case glass-melting operation.

Process Option 3 - Coal-Fired Hot Gas Generation (COHOGG)--

In this process (which is described in detail in Volume XI, pages 48-53), coal is pyrolyzed to produce a combustible gas for the glass-melting operation. Sulfur is removed directly from the process by the addition of limestone. In addition to the ash from the coal and the base case solid waste stream, this alternative generates a calcium sulfate solid waste stream. The primary increase in toxic pollutants over and above base case discharge is due to the heavy metals present in the coal ash.

Process Option 4 - All-Electric Melting--

Molten glass can be heated by the passage of an electric current. Both the design and the operation of an all-electric glass-melting furnace differ greatly from the typical natural gas-fired regenerative furnace. A detailed description of the design and operational differences is given in Volume XI, pages 53-55.

All-electric melting is based on the use of purchased electrical power, and therefore there is a shift of some of the environmental problems from the glass-manufacturing plant to the electric power generating station. This process change generates solid waste in the form of coal ash (at the power plant) and dust from the glass-melting air pollution control system (as in the base case process but probably in smaller quantity). As in the case of the other coal-based process options, the heavy metals present in the coal ash represent the major discharge of toxic pollutants to the environment.

Process Option 5 - Batch Agglomeration Preheating--

This process, still in the developmental stage, is designed to pretreat the batch ingredients rather than to conserve energy. A variation of the process proposes to use waste heat for preheating the materials. The preheating step, in itself, does not produce any waste discharges (although it does slightly alter the volume of combustion gases discharged).

If natural gas is the energy source, the nature and quantity of pollutants will be the same as the base case. If one of the coal-based alternatives is used, the previously described solid waste streams will be generated. In either case, no organic pollutants are expected and toxic pollutants would be limited to the heavy metals noted earlier.

Summary

The base case natural gas-fired melting operation discharges air, water, and solid waste streams containing heavy metals originally present in the raw materials used to manufacture the glass. The heavy metals are present in particulate form. The bulk of the heavy metal-containing particulates is eventually discharged to the environment in the solid waste stream.

The coal-based process options do not alter the emissions from the melting operation, but rather introduce additional emissions of heavy metals from the large quantities of coal ash produced. The various desulfurization steps required by the coal-based alternatives produce either either a calcium sulfate/sulfite residue (which also contains coal ash) or an elemental sulfur stream. If the Stretford process for elemental sulfur recovery is employed, a small and intermittent wastewater stream containing high concentrations of organic reagents will be produced.

A qualitative comparison of the organic/toxic pollutant discharges is presented in Table 8.

Other problems inherent in a shift away from natural gas in the glass industry, such as capital cost and product quality, are expected to play a larger role in decision-making concerning the alternative processes than would the question of organic and toxic pollutants.

CHLOR-ALKALI

Chlorine Production via the Graphite Anode Diaphragm Cell

Base Case Discharge of Organic/Toxic Pollutants--

A detailed description of the diaphragm cell process is given in Volume XII, pages 21-28. In this process, a nearly saturated solution of sodium chloride is subjected to electrolysis to yield chlorine, sodium hydroxide, and hydrogen.

TABLE 8. GLASS INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
Base case natural gas-fired glass melting	Heavy metals from particulates collected by air pollution control system. Minor source of organic/toxic pollutants.	Heavy metal-containing particulates. With proper air pollution control, minor source of organic/toxic pollutants.	Heavy metal-containing particulates removed from air and water streams. Major source of organic/toxic pollutants.
Coal gasification	Base case emissions plus small, high organic concentration wastewater stream from Stretford sulfur-removal process. Minor source of organic/toxic pollutants.	Base case emissions plus SO_2 and particulate-containing emissions from coal gasification unit. Minor source of organic/toxic pollutants.	Base case emissions plus elemental sulfur stream and large volumes of heavy metal-containing coal ash. Major source of organic/toxic pollutants.
Direct coal firing	Base case emissions plus additional coal ash containing scrubber water. Minor source of organic/toxic pollutants.	Essentially the same as the coal gasification process option.	Base case emissions plus calcium sulfate sludge from SO_2 control plus coal ash. Major source of organic/toxic pollutants.
Coal-fired hot gas generation	Same as base case.	Similar to coal gasification process option.	Base case emissions plus calcium sulfate solid waste from SO_2 control system plus coal ash. Major source of organic/toxic pollutants.

(continued)

TABLE 8 (Continued). GLASS INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
All electric melting	Same as base case.	Reduction in pollutants at the glass plant. Air emissions of the electric power plant must be taken into account.	Base case emissions plus SO_2 control sludge plus coal ash at the power plant. Major source of organic/ toxic pollutants.
Batch agglomeration - preheating	Same as base case.	Same as base case, or slightly less.	Same as base case.

Wastewater - The base case diaphragm cell chlor-alkali plant generally has the following wastewater discharges (Volume XII, pages 23, 29):

- A solution of sodium hypochlorite and sodium bicarbonate from the scrubbing of chlorine tail gas;
- Weak caustic and brine solution from the caustic evaporators that use barometric condensers;
- Weak caustic and brine solution from the caustic filter washdown; and
- Intermittent wastes from general housekeeping operations and equipment cleaning.

Lead and copper are used in the cell construction and are sometimes present in the wastewater effluents as the result of cracks around the protective resin seals which encase the lead portion of the cell.

Solid Waste - Prior to electrolysis, calcium, magnesium, and heavy metals are removed from the raw brine by adding sodium carbonate to precipitate the metals as hydroxides and carbonates. The precipitates are removed as a wet sludge and usually sent to landfill (or lagoon).

During normal processing the graphite anodes are consumed and form tiny particles which clog the diaphragm cathode. As a result, cells must be periodically rebuilt. Since the diaphragm contains asbestos, and lead is present in the cell bottoms, the debris from cell rebuilding contains lead and asbestos weighing approximately 0.04 and <0.4 lb/1000 lb, Cl_2 respectively. It is disposed of through landfill dumping.

The reactions between chlorine and organic material in the graphite anode result in the formation of volatile chlorinated organic material of rather indefinite composition. It is removed from the chlorine in a final purification step, drummed, and disposed of either by incineration or landfill. This waste amounts to 0.45 lb/1000 lb Cl_2.

Typical solid waste generation rates are given in Volume XII, page 23.

Air Emissions - Atmospheric emissions of chlorine, carbon dioxide, carbon monoxide, residual gas,or hydrogen occur from diaphragm cell plants in amounts that depend largely upon plant operation. Chlorine and other gases can escape to the atmosphere from various vents and leaks throughout the plant. Since emissions of chlorine to the atmosphere represent an economic loss, strong efforts are made to control such emissions.

When a chlorine-cell gas is compressed and cooled to produce liquid chlorine, non-condensable gases saturated with chlorine vapor are produced at the discharge of the condenser. These gases are commonly called blow gas. The value of the chlorine contained in the blow gas is significant and, for this reason, all but the smallest plants have for many years recovered chlorine by either burning it with hydrogen to make hydrochloric acid or by caustic scrubbing to produce bleach.

Process Option 1 - Dimensionally Stable Anodes (DSA)--

To eliminate the problems associated with the graphite anode, the industry has long worked on developing a non-consumable anode for use in the diaphragm cell. The dimensionally stable anode consists of an expanded titanium metal substrate coated with precious metal/rare earth oxides. The DSA has numerous advantages which result in power savings and reduced pollutional loads. The DSA leads to a major reduction in the formation of chlorinated organics as well as eliminating the need for handling and disposing of waste graphite anodes. The amount of asbestos destined for land disposal is also reduced.

The use of dimensionally stable anodes does not, in any way, alter the sludge produced from brine purification, nor does it appreciably alter air emissions or wastewater discharges.

Process Option 2 - Modified Diaphragms--

In addition to the significant changes in anodes, some major improvements are being introduced for diaphragms which have beneficial effects on both power consumption and pollution control. The three most significant modified diaphragms are: (a) polymeter modified asbestos; (b) polymer membranes; and (c) ion exchange membranes. These are described in detail in Volume XII, pages 48-52.

Polymer Modified Asbestos - Use of the polymer modified asbestos diaphragm has a minor environmental advantage over conventional asbestos diaphragms in that the discarded material, at the time of cell rebuilding, is in stabilized pieces instead of loose asbestos fibers. Thus, disposal is easier and safer because the fibers resist dispersion. The amount of brine sludge generated would be the same as in the base case, and the quantity of cell rebuilding waste would be approximately the same as in the case of the dimensionally stable anode. Air emissions and wastewater discharges would not be appreciably different from those of the base case.

Polymer Membranes and Ion Exchange Membranes - While the quantity of brine purification sludge would remain the same, the use of polymer membranes and ion exchange membranes would eliminate the graphite and asbestos rubble associated with the rebuilding on conventional diaphragm cells. Also, the generation of chlorinated hydrocarbon waste material would be virtually eliminated.

As in the case of the other process options, there would be no appreciable change in the base case air emissions or wastewater discharge.

Summary

The major discharge of organic/toxic material from the base case diaphragm cell process is the solid waste from cell rebuilding that contains asbestos and lead, and a waste stream from chlorine purification that consists of chlorinated organic compounds.

Two process options, the use of dimensionally stable anodes and the use of modified diaphragms, both alleviate the organic/toxic pollutant problem by reducing the amount of asbestos discharged. The use of modified diaphragms also virtually eliminates the chlorinated organic waste stream from the chlorine purification step. The process options do not appreciably alter the base case brine purification sludge stream, air emissions, or wastewater discharges. With the great concern over asbestos in the environment, these two processes will offer benefits in addition to the energy conservation aspect and should be encouraged. Long-term operating efficiencies and cost must still be established.

PHOSPHORUS/PHOSPHORIC ACID

Furnace Acid-Electric Furnace Production of Phosphorus and Conversion of Phosphorus to Phosphoric Acid

Base Case Discharge of Organic/Toxic Pollutants--

Phosphate rock is mined in Florida, Tennessee, and North Carolina, and in the Mountain States of the West. It is converted to commercial end-products either by digestion with sulfuric acid to produce phosphoric acid (the "wet process") or by reduction to elemental phosphorus in an electric furnace. Most of the phosphorus from the electric furnace is burned in air and the oxides absorbed in water to form phosphoric acid.

Although phosphoric acid is the principal commercial end-product of each of the two methods, there is an important difference in the purity of the acid obtained. Phosphoric acid produced via the electric furnace process is essentially a pure chemical that is suitable for detergent, food, and fine chemical uses. Wet process phosphoric acid is not pure; it is suitable for fertilizer manufacture, but, without cleanup, not for most other purposes.

The key issue in this whole analysis is the fact that the manufacture of phosphoric acid via the electric furnace process has an energy consumption per unit of product that is approximately 5 times that of the wet process. There is, therefore, an incentive to modify the wet process in order to produce phosphoric acid that has a level of purity equivalent to that produced by the electric furnace process.

In the electric furnace process (which is described in detail in Volume XIII, pages 22-34), the phosphate rock is first fed to a direct-fired rotary kiln where it is heated to a temperature of incipient fusion. It is then processed through a screening operation to a suitable size range. The kiln gases must be scrubbed to remove dust and fluorides present in the phosphate rock. The other raw materials, coke and silica, are also dried before they are fed, along with the prepared phosphate rock, into the electric arc furnace. The phosphorus is produced as gaseous P_4 and is then condensed as a liquid. The production of phosphorus and its conversion to phosphoric acid usually occur at different geographic locations. The most common practice is to ship the liquid phosphorus to the point of end-use where it is converted to phosphoric acid by oxidation and dissolution in water.

A number of toxic pollutants are present in the air emissions, wastewater effluents, and solid waste streams from the manufacture of phosphorus/phosphoric acid via the electric furnace process.

Wastewater - There are three major wastewater streams generated by the electric furnace production of elemental phosphorus:

- Nodulizer Scrubber Water Blowdown - Gaseous emissions from the phosphate rock nodulizer are dusty and contain hydrogen fluoride and silicon tetrafluoride; therefore, they must be controlled by means of a wet scrubber. The scrubber water is recycled. The necessary purge stream from the recycle system is acidic, contains phosphates, sulfates, fluorides, and suspended solids, and must be treated prior to discharge.

- Slag Quench Water - Furnace slag is cooled by means of quenching with a water stream. The slag quench water is slightly alkaline, contains phosphates, sulfates, fluorides, and suspended solids, and also must be treated.

- "Phossy" Water - A notoriously difficult stream is the so-called "phossy" water. This stream results from the unavoidable contact of liquid phosphorus with water in the condenser and in the phosphorus transfer lines. Water is also used as a seal in storage and transport to prevent exposure of the phosphorus to air. The result is that water discharged from these operations contains a small amount of very finely divided phosphorus in suspension. The "phossy" water also contains significant amounts of phosphates and fluorides.

The usually recommended method of treatment for the above wastewater streams consists of the addition of lime for the neutralization of acidity and the precipitation of fluorides and phosphates followed by coagulation and settling for the removal of suspended solids (including particles of elemental phosphorus) and precipitates. With proper treatment the wastewater should contain relatively

low concentrations of fluorides, phosphates, and phosphorus, although improvements in fluoride removal are still being sought.

Solid Waste - There are a number of solid waste streams produced by the overall production of phosphoric acid via the electric furnace process.

- Slag - Large quantities of slag are produced. The slag contains silica, iron oxide, calcium oxide, calcium fluoride, alumina, and the oxides of trace heavy metals. It is sold as a construction material and therefore does not become a waste stream destined for disposal.

- Wastewater Treatment Sludge - The treatment of the wastewater stream, as described in the preceding sections, produces a waste sludge containing calcium fluoride, calcium phosphate, calcium sulfate, elemental phosphorus, and the hydroxides of trace heavy metals (including arsenic).

Care should be taken to dispose of the sludge in an environmentally acceptable manner. The presence of elemental phosphorus and trace arsenic compounds can result in low-level emissions of volatile species, such as the phosphorus oxides and arsine. Leaching from landfill lagoons must be avoided.

Air Emissions - Air pollution control is a significant problem in a phosphorus plant. Large amounts of dust originating from the phosphate rock are generated by the various processing steps. A variety of air pollution control devices is used. However, no air pollution control system is 100% effective, and the particulates that do escape contain fluorine compounds, phosphates, and other constituents originally present in the phosphate rock.

Process Option 1 - Wet Process Production of Phosphoric Acid Followed by Chemical Cleanup--

As previously stated there are a number of impurities in wet process phosphoric acid which make it unsuitable for use as detergent phosphate. These impurities include calcium chloride, iron and aluminum salts, carbon and organic matter, and small quantities of a number of heavy metals, such as magnesium, chromium, titanium, manganese, copper, zinc, arsenic, vanadium, and uranium. The acid is saturated in calcium sulfate and has a high content of fine suspended solids. It is difficult to remove these impurities to the degree necessary to meet specifications for food grade or fine chemical phosphate use. A major outlet for phosphoric acid, however, is in the form of sodium tripolyphosphate (STPP). Wet process acid can be purified to the degree necessary for this product by a two-stage neutralization cleanup process, as described in Volume XIII, pages 48-60.

This alternative produces a variety of wastewater effluents, solid waste streams, and air emissions, which are described below:

Wastewater - The main wastewater stream from the wet process production of phosphoric acid remains the overflow from the gypsum ponds (the large impounded areas containing the acid-insoluble fraction of the phosphate rock). The liquid fraction of this residue contains sodium silicofluoride, phosphates, free phosphoric acid, and a number of trace heavy metals, such as cadmium. When the recommended treatment (consisting of lime addition followed by precipitation and sedimentation) is applied, the treated effluent should contain relatively low concentrations of the above pollutants, although further improvements are still desired.

Solid Waste - The following solid waste streams are generated:

- Gypsum Sludge - The wet process produces very large amounts of gypsum sludge from the reaction of sulfuric acid with the phosphate rock. The sludge is stored in large impoundments which also serve as water recirculation reservoirs. A large amount of the fluorine originally present in the phosphate rock is discharged, along with the gypsum, as sodium silicofluoride. The gypsum sludge contains free phosphoric acid and trace heavy metals, and is slightly acidic.

- Wastewater Treatment Sludge - When gypsum pond overflow is treated with lime, a waste sludge containing calcium fluoride, calcium phosphate, and the hydroxides of trace heavy metals is produced.

- Impurities From the Two-Stage Neutralization Cleanup Step - The impurities from the two-stage cleanup step consist of filter cakes containing sodium silicofluoride in both the aqueous and solid phases, phosphoric acid, calcium sulfate, ferric phosphate, aluminum phosphate, and trace quantities of heavy metals.

Air Emissions - Air emissions associated with the production of phosphoric acid via the wet process are generated by both the digestion and evaporation systems. The uncontrolled air emissions contain hydrogen fluoride and silicon tetrafluoride. Wet scrubbers remove most of these contaminants, and, in turn, produce a contaminated wastewater stream which, itself, must be neutralized.

The chemical cleanup of wet process phosphoric acid produces a number of small air emissions which are relatively uncontaminated.

Process Option 2 - Wet Process Production of Phosphoric Acid Followed by Solvent Extraction Cleanup--

In this process (which is described in detail in Volume XIII, pages 60-71), phosphate rock is dissolved in hydrochloric acid rather than in sulfuric acid. The crude phosphoric acid thus produced is subjected to a solvent extraction step in which the phosphoric acid is transferred from solution in an aqueous phase to solution in an organic phase, such as normal butanol, leaving behind the undesirable impurities, such as calcium chloride, in the aqueous phase. The organic phase can then be contacted in a separate unit with fresh water to yield a pure solution of phosphoric acid. The calcium chloride brine initially separated from the extraction step also contains hydrochloric acid and solvent which must be recovered.

Since the process is still in the developmental stage at this time, it is only possible to speculate as to the nature of the wastewater effluents, solid waste streams, and air emissions.

With respect to wastewater effluents and solid waste disposal, the most significant difference between this process and the conventional wet process followed by chemical cleanup is that a large concentrated calcium chloride brine stream is substituted for a large fraction of the gypsum sludge stream. Undissolved inorganic solids separated from the digestor liquor would be impounded in much the same way as in the conventional process. Since much of the solid waste would be replaced by calcium chloride brine, the size of the impoundments would be considerably smaller.

The impoundment overflow would have to be treated in much the same way as in the conventional process, i.e., via lime treatment to neutralize acidity and to precipitate fluoride, phosphate, and metals. It should be noted that solvent (normal butanol) losses within the process will eventually appear in the liquid fraction of the sludge. If solvent losses are severe, the liquid fraction of the sludge could exert a significant biochemical oxygen demand. This entire process presents serious water pollution control problems, since chloride salts of metals tend to be soluble.

Air emissions are similar to those of the conventional wet process, with the exception of the anticipated losses of the normal butanol solvent. However, butanol is not considered a toxic material.

Process Option 3 - The Use of Byproduct Sulfuric Acid--

A conventional wet process plant for phosphoric acid consists of two distinct process units. In the first, sulfur is converted to sulfuric acid; in the second, sulfuric acid is used as a reagent to convert phosphate rock to phosphoric acid. Sulfur is a major element of the production of phosphoric acid, and, at the right price, a phosphoric acid producer would be tempted to use byproduct sulfuric acid (obtained

largely from electric power plant sulfur dioxide control systems) in place of the sulfur.

While the use of byproduct sulfuric acid will eliminate that part of the pollution problem associated with an on-site sulfuric acid plant, it will have a negligible effect on both the quantity and characteristics of the waste streams (and the presence of organic/toxic pollutant) associated with the overall manufacture of phosphoric acid.

Process Option 4 - Strong Phosphoric Acid Processes--

Although these processes (which are described in detail in Volume XIII, pages 73-75) provide certain operational and economic advantages, it is not apparent that they influence the discharge of organic/toxic pollutants one way or another.

Summary

The base case process for producing high-grade phosphoric acid via the electric furnace production of elemental phosphorus and subsequent conversion to phosphoric acid generates: (1) a wastewater stream containing fluorides, phosphates, and elemental phosphorus; (2) solid waste streams consisting of fluoride-containing slag, and wastewater treatment sludge that contains fluorides, phosphates, elemental phosphorus, and heavy metals; and (3) air emissions containing fluorine compounds, phosphates, and other constituents originally present in the phosphate rock. The slag is sold as a construction material.

The process option involving the wet process production of phosphoric acid followed by chemical cleanup differs from the base case, mainly in that large amounts of wet gypsum sludge (as opposed to dry slag) are produced. The gypsum sludge contains fluorides, phosphates, and trace heavy metals. The cleanup step produces a solid residue which also contains fluorides, phosphates, and heavy metals.

The process option involving the hydrochloric acid-based wet process followed by solvent extraction cleanup differs considerably from the conventional process in that a large calcium chloride brine stream is substituted for a large fraction of the gypsum sludge stream. Pollutants associated with the base case, i.e., fluorides, phosphates, and heavy metals, are also present, as well as lost solvent consisting of normal butanol. The water pollution problems associated with this process option are considered quite serious, and are certainly worse than those of the base case. In view of these observations, the chemical cleanup processes will require careful evaluation and assessment to assure proper environmental protection in spite of the attraction of significant energy conservation which they offer.

The process option involving the use of byproduct sulfuric acid and the option based on the strong phosphoric acid process have a negligible impact on the discharge of organic/toxic pollutants.

PRIMARY COPPER

Manufacture of Copper by Smelting and Refining of Concentrates

Base Case Discharge of Organic/Toxic Pollutants--

Copper extraction from sulfide ores is traditionally divided into four segments:

- Mining - where ore containing 0.6% to 2% copper is mined;
- Beneficiation - where the copper-containing minerals are separated from the waste rock to produce a concentrate containing about 25% copper;
- Smelting - where concentrates are melted and reacted to produce 98% pure "blister" copper or "anode" copper (copper 98% to 99% pure requiring further refining); and
- Refining - where blister copper is refined electrolytically to produce 99.9% pure "cathode" copper.

The energy-related process changes described in Volume XIV affect only the smelting and refining portions of copper extraction; therefore, conventional smelting and refining represent the base case against which potential process options have been compared in order to evaluate pollutional and energy consequences of these process alternatives.

Conventional smelting of sulfide concentrate involves the smelting of concentrates in a reverberatory furnace either directly (green charge smelting) or after roasting (calcine smelting). The mixture of molten sulfides from the reverb is converted to blister copper in convertors.

Conventional electrorefining purifies the smelter output to cathode quality copper. A detailed description of the conventional smelting and refining processes is presented in Volume XIV, Appendix A.

Although the conventional smelting and refining of copper concentrates do not involve the discharge of organic pollutants, metals such as arsenic, antimony, bismuth, mercury, lead, zinc, and tellurium can be present in air, water, and solid waste streams. The heavy metals are not externally introduced into the process, but rather originate from the copper ore itself.

Most of the heavy metals removed from the copper ore during the refining process are in the form of a slag containing low solubility metal oxides. Although very large quantities of slag are produced, it is a rather inert, rock-like material, and in itself would not generally be considered any more toxic than the original ore.

A number of wastewater streams are produced in the smelting and refining of copper. The wastewater is acidic, contains high amounts of suspended solids, and also contains low levels of soluble heavy metals. The recommended means of treatment for meeting the proposed 1983 effluent guidelines include neutralization and sedimentation, both of which produce a waste sludge. The sludge would contain calcium sulfate and a variety of metal hydroxides. Although the quantity of wastewater treatment sludge that would be produced is far less than the quantity of slag, the finely divided precipitates composed of metal hydroxides would be more subject to the leaching of heavy metals than would the slag. When properly treated, the wastewater stream should contain heavy metals in concentrations no greater than several parts per million.

The smelting of copper produces large quantities of dust composed of fractions of the ore itself and therefore containing heavy metals. Most of the dust is collected by air pollution control devices and then recycled to the reverberatory furnace. To prevent the buildup of impurities, it is necessary to purge a portion of the recycled dust from the system. Depending on the composition of the feed, a fraction of the dust may either be sold to other specialized smelters or disposed of as a solid waste.

Since no air pollution control device is 100% effective in removing particulate matter, it is inevitable that copper smelters will discharge a certain amount of heavy metal-containing particulate matter to the atmosphere. Metals that are easily volatilized, such as arsenic, lead, and zinc, tend to form very fine condensation particles that are not easily removed by many conventional air pollution control devices. Although the quantity of metals discharged to the atmosphere is many times less than the amount discharged as a solid waste, it still constitutes a not insignificant pollutional problem, particularly since it will be emitted as extremely fine particulates. Sulfur oxides, of course, are another problem requiring attention.

Process Option 1 - Outokumpu Flash Smelting--

Flash smelting (which is described in detail in Volume XIV, pages 41-44) combines the separate roasting and smelting operations of conventional copper extraction into a combined roasting-smelting process. The heat generated by the exothermic roasting reactions can be used for smelting so that little or no extraneous fuel is needed. A characteristic of this method is that fine-grained concentrates are used and the smelting takes place in suspension, which allows for rapid reaction rates. The major advantages of the method are a reduction in fuel used for smelting and the production of a stream of gas high in SO_2 which is suitable for sulfuric acid manufacture.

The Outokumpu flash smelting process produces the same quantity of slag and bleed dust as the conventional smelting and refining of copper. Since the water pollution control problems are similar to those of a conventional smelter, it is reasonable to assume that if the same

recommended treatment technology is applied to the Outokumpu process, the same quantity of wastewater treatment sludge will be generated.

While the Outokumpu process has several advantages regarding SO_2 control, it is not apparent that the emission of heavy metal-containing particulates would be substantially different from that of the base case smelting process.

Process Option 2 - The Noranda Process--

The Noranda process combines the three operations of roasting, smelting, and converting of copper concentrates in a single reactor. The heat losses suffered during the transfer of concentrate from the roaster to the reverberatory furnace are suppressed, as well as the heat losses occurring during the transfer of matter from the reverberatory furnace to the convertor. In addition, the net heat of oxidation is used for smelting. A detailed process description is presented in Volume XIV, pages 55-70. Other than expected reductions in SO_x emissions, the air, water, and solid wastes generated by the process are not expected to be significantly different in heavy metal levels from those generated by conventional smelting.

Process Option 3 - The Mitsubishi Process--

The Mitsubishi process consists of three metallurgical stages, each of which is carried out in a separate furnace. Thus, there is a smelting furnace for concentrates, a converting furnace to oxidize iron in the matte and make blister copper, and a slag cleaning furnace. Intermediate products in the molten state move continuously among the respective furnaces which are thus functionally connected with each other. A detailed process description is presented in Volume XIV, pages 71-81. The Mitsubishi process has many of the same energy-conserving advantages as the Outokumpu and Noranda processes. The air, water, and solid waste streams are expected to be quite similar to those from the Outokumpu process.

Process Change 4 - The Use of Oxygen in Smelting--

Copper smelting by any of the foregoing base or new processes can be conducted with pure oxygen or by using oxygen-enriched air. Reasons for using oxygen or oxygen enrichment include:

- Increasing processing temperatures and process heat rates;
- Decreasing the nitrogen content of the flue gases (when high SO_2 concentrations are needed) and increasing fuel efficiency (particularly where waste heat is not recovered); and
- Increasing the specific capacity of furnaces so that production of metal is increased for a given size reactor.

We do not believe that the use of oxygen in smelting will significantly alter the base case air, water, or solid waste discharges. The on-site oxygen plant would require large volumes of water which, if recycled through a cooling tower, would very likely contain small quantities of corrosion inhibitors such as chromium compounds. The oxygen plant consumes electricity, and the generation of this electricity at a central power station has associated pollutional loads, such as the disposal of coal ash and SO_2 removal sludge which should also be considered.

Process Option 5 - Metal Recovery from Slag--

In conventional copper smelting, convertor slag is recycled to the reverberatory furnace, and all of the slag tapped from the furnace is discarded. The copper contained in this discarded slag is lost. The amount of copper lost with the slag is quite significant--about 1.5% to 3% or more of the copper in the feed materials.

Slag can be recovered by two methods: (1) flotation, or (2) slag cleaning the electric furnaces.

Flotation - In flotation, the slag is acid ground and the copper is recovered via froth flotation (see Volume XIV, pages 89-93). This process converts the slag into fine particles which are then disposed of as a wet slurry into a tailings pond. The water from the tailings pond is recycled. This process has no effect on the base case air emissions or wastewater effluent loadings. While the overall quantity of slag is not radically different from that of the base case conventional smelter, and its copper content will be lower, it will be in the form of very fine particles mixed with water rather than large dry particles. Consequently, concern over leachability of trace heavy metals should be greater.

Slag Cleaning in Electric Furnace - The mechanism by which slag can be recovered in an electric furnace is discussed in Volume XIV, pages 93-95. The fumes coming off the electric furnace must be collected, and the dusts are further processed for recovery of metallic values (zinc, cadmium, etc.). The volume of the cleaned gas is insignificant and can be easily merged with other air streams. Aside from reducing the metal content of the slag, this practice does not alter the quantity or nature of the base case solid waste streams.

Process Option 6 - The Arbiter Process--

The Arbiter process is one of several potentially applicable hydrometallurgical copper extraction techniques.

The basic process (which is described in detail in Volume XIV, pages 95-106) consists of five separate stages for the treatment of copper concentrates. The copper concentrate slurry is first leached with ammonia and oxygen. The pregnant solution is then separated from

the leached solids. From there it is sent to a solvent extraction step where copper is selectively extracted with an organic reagent to form a copper-loaded electrolytic solution. Copper is recovered from the solution via conventional electro-winning. The actual process entails a large number of rather complex material recycle circuits and purification steps.

The Arbiter process, like most hydrometallurgical processes, causes little direct air pollution. The major emissions from the process are associated with the ammonia recovery system, which would contain traces of ammonia and fugitive emissions of sulfuric acid mist from the electro-winning tank house. Unlike the base case technology, there are no major emissions of heavy metal-containing particulates.

The process is energy-intensive and mainly uses electricity and steam. Some pollution would be associated with the boiler plant in both cases whether on- or off-site.

The Arbiter process can be operated so that there is no wet aqueous discharge to the environment in areas where solar evaporation is high, such as Arizona, the location considered for this study. In areas where evaporation is insufficient, it might be necessary to bleed water from the process and treat it in a manner similar to that recommended for conventional copper smelters.

The Arbiter process produces two major solid waste streams:

Gypsum Sludge - During the process, ammonia is recovered from spent ammonium sulfate streams by boiling with lime to yield ammonia and gypsum (calcium sulfate). The gypsum sludge forms a major solid waste stream.

Leach Residue - The process produces a leach residue containing iron oxide, silica, pyrites, bismuth, sulfides, lead, arsenic, and other metals.

These two waste streams would require storage in lined ponds with a wet top surface to prevent dust emissions during the period the pond is in use and proper cover after the pond is abandoned.

The total solid waste stream is substantially greater than that of the base case process, although the quantity of heavy metals present would be roughly the same. The extent to which byproduct metals can be recovered when using the Arbiter process is not well established. The wet sludge and leach residue are probably more subject to the leaching of heavy metals than the relatively inert slag from the base case process.

Summary

There is no discharge of organic pollutants from the base case conventional smelting and refining process. Heavy metals, mostly in the form of particulate matter, are present in air, water, and solid waste streams. By far, the solid waste--in the form of slag, dust, and wastewater treatment sludge--constitutes the major source of heavy metals discharged to the environment.

The discharge of heavy metals into the air, water, and solid waste streams of the Outokumpu, Noranda, and Mitsubishi processes is essentially the same as that of the base case technology.

Aside from an incremental pollutional load associated with off-site power generation and the use of cooling towers, the use of oxygen in smelting does not alter the base case pollutional load.

The only major pollutional implication of recovering metal from slag is that the slag destined for disposal will have a lower concentration of copper and certain other metals.

The Arbiter process has major pollutional implications. It virtually eliminates the air pollution problem associated with conventional smelting, but substantially increases the amount of solid waste destined for disposal. The solid waste is in the form of a wet sludge rather than a hard dry slag and is, therefore, more subject to the leaching of heavy metals. This process will need careful evaluation of pollution potential in conjunction with its progress through development.

A qualitative comparison of the organic/toxic pollutant discharges for the several processes is presented in Table 9.

FERTILIZER

The Manufacture of Nitric Acid

Base Case Discharge of Organic/Toxic Pollutants--

Of the major fertilizer production activities (excluding the production of ammonia which is covered as a separate industry in Volume VII), the manufacture of nitric acid poses the greatest number of possible conflicts between energy conservation and pollution control. The problem areas are in the control of gaseous nitrogen oxide emissions rather than in the manufacturing process itself. The basic process and the several control technologies now being considered are described in Volume XV, pages 24-42.

Nitric acid is an important material in the manufacture of fertilizer-grade ammonium nitrate and explosives. The acid is produced by the oxidation of ammonia, usually under high pressure and temperature over a platinum catalyst, forming nitric oxide (NO). The gaseous products from the reactor and oxygen are cooled to form NO_2, and are then sent to an absorption tower to form the acid product.

TABLE 9. PRIMARY COPPER INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
Base case conventional smelting and refining of concentrates	Low levels of soluble heavy metals in treated wastewater effluent. Minor source of organic/toxic pollutants.	Fine particulates containing heavy metals. With adequate air pollution control, minor source of organic/toxic pollutants.	Very large quantities of heavy metal-containing slag, dust, and wastewater treatment sludge. Metals, mostly in solid phase. Major source of organic/toxic pollutants.
Outokompu flash smelting	Similar to base case.	Similar to base case.	Similar to base case.
The Noranda process	Similar to base case.	Similar to base case.	Similar to base case.
The Mitsubishi process	Similar to base case.	Similar to base case.	Similar to base case.
The use of oxygen in smelting	Base case waste load plus cooling tower blowdown (possibly containing chromium) and external pollution loads associated with fossil fuel-burning control power station.	Base case waste load plus air pollution associated with fossil fuel-burning central power station.	Base case waste load plus solid waste stream (coal ash and SO_2 control sludge) associated with fossil fuel-burning central power station.
Metal recovery from slag	Similar to base case.	Similar to base case.	Lower concentration of copper and certain other heavy metals in waste slag.

(continued)

TABLE 9 (Continued). PRIMARY COPPER INDUSTRY
QUALITATIVE COMPARISON OF ORGANIC/TOXIC POLLUTANT DISCHARGES

Process	Medium		
	Water	Air	Solid Waste
The Arbiter process	Depending on site specific conditions, treated effluent loads very likely to be similar to base case.	Virtual elimination of air pollution problems associated with base case.	Substantial increase in quantity of solid waste. Solid waste is in the form of a wet sludge and contains heavy metals in a form more likely to be leached than that of the base case. Major source of organic/toxic pollutants.

The only significant pollutional problem resulting from the production of nitric acid is the discharge of unabsorbed oxides of nitrogen in the absorption tower tail gas.

While each of the several processes available for the control of nitrogen oxide emissions has significant energy and NO_x air control implications, none produces waste streams containing organic/toxic pollutants.

Mixed Fertilizer Plants

Base Case Discharge of Organic/Toxic Pollutants--

The base case plant used in this analysis is an ammoniation granulation plant (ammoniation of normal super phosphate) equipped with a natural gas-fired dryer and bag house filter to control particulate emissions. There are no contaminated wastewater streams or solid waste streams, and the collected particulates actually consist of product material and are recycled back into the process. No organic/toxic pollutants are discharged from the base case process.

Process Option - Conversion from Natural Gas to Fuel Oil and Installation of a Wet Scrubber for Air Pollution Control--

Due to the impending shortage of natural gas, there is an incentive to convert drying operations from natural gas to fuel oil. When using fuel oil, however, there is a tendency for bag house filters to become clogged with products of incomplete combustion. While it may be possible to alleviate this problem by modifying the combustion process, it is likely that many plants would require a wet scrubber.

Even though it is possible to recycle scrubber water to a high degree, a certain amount must be purged to prevent the excessive buildup of dissolved solids. The scrubber water would contain ammonia, chloride, fluoride, phosphate, and suspended solids. It would most likely have to be treated with lime to precipitate the fluoride and phosphate as calcium fluoride and calcium phosphate, and to convert ammonium ions to ammonia gas so that it could be stripped from the wastewater by aeration. The wastewater treatment system would produce a waste sludge composed of calcium phosphate and calcium fluoride. The liquid fraction of the sludge would contain small amounts of dissolved phosphate, fluoride, and possibly some ammonia, which would represent the most environmentally objectionable constituents. Although the pollutional problems associated with this process option are clearly greater than the base case, the waste streams do not contain pollutants now considered toxic.

Summary

There is no discharge of organic/toxic pollutants from the base case nitric acid plant, nor from the various process options intended for the control of NO_x emissions. This aspect will not play a role in the industry's selection of control technology.

The base case mixed fertilizer plant has no discharge of organic/toxic pollutants. The process option involving the conversion from natural gas to fuel oil will likely result in wastewater and solid waste discharges containing phosphates, fluorides, and ammonia, but no organic/toxic pollutants.

REFERENCES

U. S. Environmental Protection Agency, "Characterization of Sulfur Recovery from Refinery Fuel Gas," EPA-450/3-74-055.

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